IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

CALLAWAY GOLF COMPANY, Plaintiff, v. ACUSHNET COMPANY, Defendant.	C.A. No. 06-

COMPLAINT AND DEMAND FOR JURY TRIAL

For its Complaint, Plaintiff alleges:

PARTIES

1. Plaintiff Callaway Golf Company ("Callaway Golf") is a corporation organized and existing under the laws of the State of Delaware, having a principal place of business in Carlsbad, California.

2. Callaway Golf is the parent company of The Top-Flite Golf Company ("Top-Flite"), which is a corporation organized and existing under the laws of the State of Delaware, having a principal place of business in Chicopee, Massachusetts.

3. Defendant Acushnet Company ("Acushnet"), upon information and belief, is a corporation organized and existing under the laws of the State of Delaware, having a principal place of business in Fairhaven, Massachusetts.

4. Acushnet, upon information and belief, is a wholly-owned operating company of Fortune Brands, Inc. ("Fortune Brands").

5. Fortune Brands, upon information and belief, is a publicly-traded corporation

organized and existing under the laws of the State of Delaware, having a principal place of business in Lincolnshire, Illinois.

JURISDICTION AND VENUE

6. This Court has subject matter jurisdiction under 28 U.S.C. §§ 1331 and 1338(a).

7. Acushnet is subject to personal jurisdiction in this District because, upon information and belief, Acushnet is a Delaware corporation and is doing and has done substantial business in this District, including business relating to the sale and distribution for sale of the infringing products as described below.

8. Venue is proper in this judicial district pursuant to 28 U.S.C. § 1400(b).

9. Callaway Golf is the owner, by assignment, of United States Patent Nos. 6,210,293, 6,503,156, 6,506,130 and 6,595,873 (the "'293, '156, '130 and '873" patents, respectively).

BACKGROUND

10. In 2003, Callaway Golf acquired the intellectual property assets of Top-Flite's predecessor-in-interest, then also known as "The Top-Flite Golf Company," and before that as "Spalding Sports Worldwide, Inc."

11. Among the assets Callaway Golf acquired was a family of patents that cover a unique blend of materials and properties for golf balls (collectively "the Sullivan patents").

12. The Sullivan patents disclose technological breakthroughs relating to golf ball construction, particularly the use of a polyurethane cover on a multi-layer solid-core golf ball, resulting in performance that had previously eluded the industry

13. The Sullivan patents include, but are not limited to, the '293, '156, '130 and '873

patents.

14. The technology claimed in the Sullivan patents revolutionized the game of golf. In fact, within two years of introduction, the vast majority of professional golfers on the PGA Tour had switched from older golf ball constructions to those incorporating the claimed technology. Some commentators have noted that the technology in the Sullivan patents has done more to change the game of golf than any other equipment advance in the history of the game.

15. Golf balls with the patented technology offer superior performance, including longer distance, better feel, and improved wear resistance, compared to prior art golf balls.

16. Callaway Golf and Top-Flite have both had success selling golf balls embodying this technology, including the Callaway Golf® Rule 35®, CTU 30 and Callaway Golf® HX® series of golf balls, the Ben Hogan® series of golf balls, and the Strata® Tour Ace™, Strata® Tour Premier™ and Top-Flite® Strata® TL-Tour™ lines of golf balls.

17. Acushnet makes and sells golf balls under the Titleist® brand.

18. Among these balls are the Titleist Pro V1®, Titleist Pro V1x™, and Titleist Pro V1*™ (collectively "the Pro V1 balls").

19. Acushnet has had great success selling the Pro V1 balls. Acushnet has sold almost a billion dollars' worth of Pro V1 balls since 2000 by incorporating the technology disclosed in the Sullivan patents. Based upon publicly available data, Callaway Golf estimates that Acushnet continues to sell Pro V1 balls at a rate in excess of $200 million per year.

20. Acushnet touts the Pro V1 balls as the best selling golf balls of all time, and as "The #1 Ball in Golf."

21. The Pro V1 balls embody the technology of the Sullivan patents, and in particular,

embody one or more claims of each of the '293, '156, '130 and '873 patents.

22. Acushnet has no credible defense to Callaway Golf's infringement claims. Instead, realizing that Callaway Golf was prepared to enforce its rights, Acushnet preemptively filed a request for re-examination of the Sullivan patents with the United States Patent and Trademark Office ("PTO"). In that request, Acushnet claims that prior art already disclosed or discussed by Top-Flite in the applications that matured into the Sullivan patents somehow presents new issues of patentability. Moreover, the prior art Acushnet now claims raises new issues of patentability for the Sullivan patents is the same art that Acushnet dismissed in its own arguments to the PTO when it was belatedly seeking a patent on virtually the same technology -- almost four years after the first Sullivan application was filed.

COUNT I - INFRINGEMENT OF THE '293 PATENT

23. Callaway Golf incorporates and realleges the allegations of paragraphs 1 through 22 as if fully set forth herein.

24. Callaway Golf is the owner by assignment of United States Patent No. 6,210,293, entitled "Multi-layer golf ball" ("the '293 patent"), which was duly and legally issued by the United States Patent and Trademark Office on April 3, 2001. A copy of the '293 patent is attached as Exhibit A to this Complaint.

25. Acushnet has infringed and both induced and contributed to the infringement of one or more claims of the '293 patent by making, using, selling and/or offering to sell infringing golf balls, including without limitation its Pro V1 balls.

26. Acushnet has and has had actual notice of the '293 patent.

27. Acushnet has and has had constructive notice of the '293 patent pursuant to

35 U.S.C. § 287(a).

28. Acushnet's infringement of the '293 patent has been and continues to be willful.

COUNT II - INFRINGEMENT OF THE '156 PATENT

29. Callaway Golf incorporates and realleges the allegations of paragraphs 1 through 22 as if fully set forth herein.

30. Callaway Golf is the owner by assignment of United States Patent No. 6,503,156 B1, entitled "Golf ball having multi-layer cover with unique outer cover characteristics" ("the '156 patent"), which was duly and legally issued by the United States Patent and Trademark Office on January 7, 2003. A copy of the '156 patent is attached as Exhibit B to this Complaint.

31. Acushnet has infringed and both induced and contributed to the infringement of one or more claims of the '156 patent by making, using, selling and/or offering to sell infringing golf balls, including without limitation its Pro V1 balls.

32. Acushnet has and has had actual notice of the '156 patent.

33. Acushnet has and has had constructive notice of the '156 patent pursuant to 35 U.S.C. § 287(a).

34. Acushnet's infringement of the '156 patent has been and continues to be willful.

COUNT III - INFRINGEMENT OF THE '130 PATENT

35. Callaway Golf incorporates and realleges the allegations of paragraphs 1 through 22 as if fully set forth herein.

36. Callaway Golf is the owner by assignment of United States Patent No. 6,506,130 B2, entitled "Multi-layer golf ball" ("the '130 patent"), which was duly and legally issued by the

United States Patent and Trademark Office on January 14, 2003. A copy of the '130 patent is attached as Exhibit C to this Complaint.

37. Acushnet has infringed and both induced and contributed to the infringement of one or more claims of the '130 patent by making, using, selling and/or offering to sell infringing golf balls, including without limitation its Pro V1 balls.

38. Acushnet has and has had actual notice of the '130 patent.

39. Acushnet has and has had constructive notice of the '130 patent pursuant to 35 U.S.C. § 287(a).

40. Acushnet's infringement of the '130 patent has been and continues to be willful.

COUNT IV - INFRINGEMENT OF THE '873 PATENT

41. Callaway Golf incorporates and realleges the allegations of paragraphs 1 through 22 as if fully set forth herein.

42. Callaway Golf is the owner by assignment of United States Patent No. 6,595,873 B2, entitled "Multi-layer golf ball" ("the '873 patent"), which was duly and legally issued by the United States Patent and Trademark Office on July 22, 2003. A copy of the '873 patent is attached as Exhibit D to this Complaint.

43. Acushnet has infringed and both induced and contributed to the infringement of one or more claims of the '873 patent by making, using, selling and/or offering to sell infringing golf balls, including without limitation its Pro V1 balls.

44. Acushnet has and has had actual notice of the '873 patent.

45. Acushnet has and has had constructive notice of the '873 patent pursuant to 35 U.S.C. § 287(a).

46. Acushnet's infringement of the '873 patent has been and continues to be willful.

PRAYER FOR RELIEF

WHEREFORE, Callaway Golf prays:

1. That this Court enjoin Defendant, its agents and employees, and any others acting in concert with it, from infringing, inducing the infringement of, or contributing to the infringement of U.S. Patent Nos. 6,210,293, 6,503,156, 6,506,130 and 6,595,873;

2. That this Court award Callaway Golf its damages resulting from Defendant's infringement, including lost profits on certain sales and a reasonable royalty on others;

3. That this Court award Callaway Golf treble damages as a result of Defendant's willful misconduct;

4. That this Court declare this case an exceptional case pursuant to 35 U.S.C. § 285; and

5. That this Court award Callaway Golf its costs and attorneys' fees and such other relief as is just.

JURY DEMAND

Callaway Golf demands trial by jury.

FISH & RICHARDSON P.C.

Date: February 9, 2006

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Exhibit A

US006210293B1

(12) **United States Patent**
Sullivan

(10) **Patent No.:** **US 6,210,293 B1**
(45) **Date of Patent:** **Apr. 3, 2001**

(54) **MULTI-LAYER GOLF BALL**

(75) Inventor: **Michael J. Sullivan**, Chicopee, MA (US)

(73) Assignee: **Spalding Sports Worldwide, Inc.**, Chicopee, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/470,196**

(22) Filed: **Dec. 21, 1999**

Related U.S. Application Data

(63) Continuation of application No. 08/870,585, filed on Jun. 6, 1997, which is a continuation of application No. 08/556,237, filed on Nov. 9, 1995, now abandoned, which is a continuation-in-part of application No. 08/070,510, filed on Jun. 1, 1993, now abandoned.

(51) **Int. Cl.**^{7} **A63B 37/12**
(52) **U.S. Cl.** **473/374**

(58) **Field of Search** 473/370–378

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,431,193	*	2/1984	Nesbitt	473/374
5,068,151	*	11/1991	Nakamura	473/377
5,314,187	*	5/1994	Proudfit	473/374

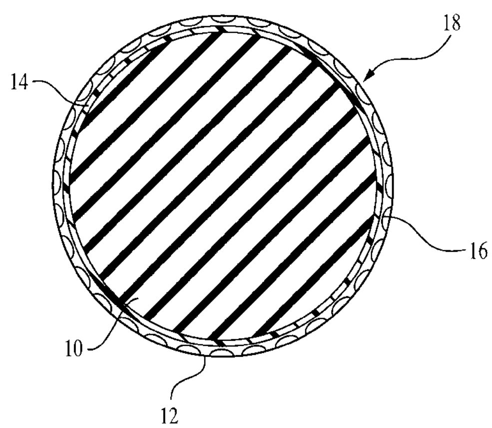
* cited by examiner

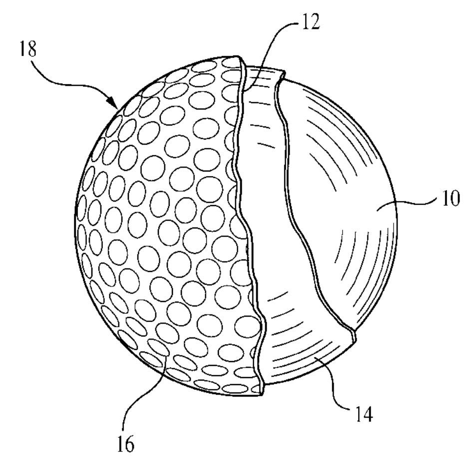
Primary Examiner—Mark S. Graham

(57) **ABSTRACT**

The present invention is directed to an improved multi-layer golf ball comprising a core, an inner cover layer and an outer cover layer. The inner cover layer is comprised of a low acid ionomer blend which may or may not include a filler such as zinc-stearate. The outer cover layer is comprised of a soft, non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane, polyester or polyesteramide. The resulting multi-layered golf ball of the present invention provides for enhanced distance without sacrificing playability or durability when compared to known multi-layer golf balls.

8 Claims, 1 Drawing Sheet





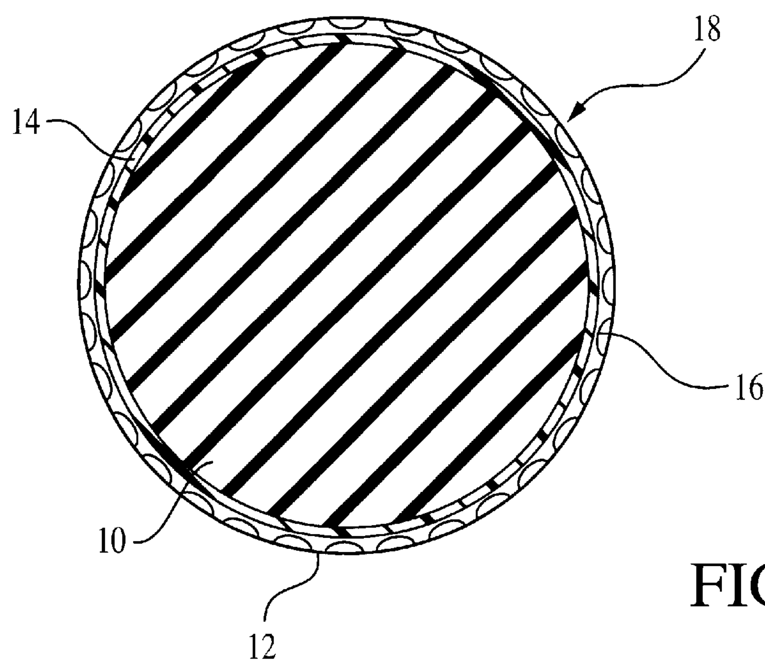


FIG. 1

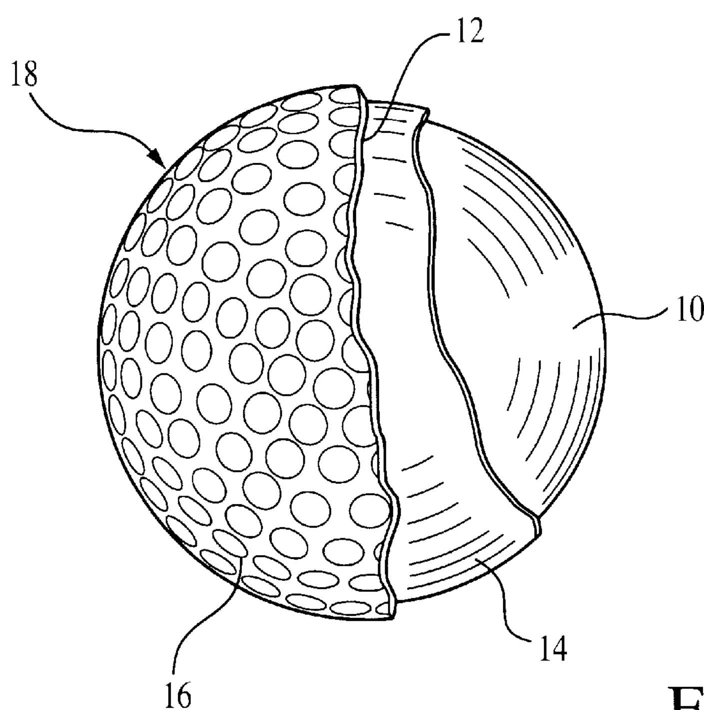


FIG. 2

MULTI-LAYER GOLF BALL

This application is a continuation application of U.S. application Ser. No. 08/870,585 filed Jun. 6, 1997, pending, which is a continuation application of U.S. application Ser. No. 08/556,237 filed on Nov. 9, 1995, now abandoned, which is a continuation-in-part of U.S. application Ser. No. 08/070,510 filed Jun. 1, 1993, abandoned.

FIELD OF THE INVENTION

The present invention relates to golf balls and, more particularly, to improved standard and oversized golf balls comprising multi-layer covers which have a comparatively hard inner layer and a relatively soft outer layer such as that produced by the use of a polyurethane based outer layer. The improved multi-layer golf balls provide for enhanced distance and durability properties over single layer cover golf balls while at the same time offering enhanced "feel" and spin characteristics generally associated with soft balata and balata-like covers of the prior art.

BACKGROUND OF THE INVENTION

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Moreover, the soft balata covers produce a soft "feel" to the low handicap player. Such playability properties (workability, feel, etc.) are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata, balata covered golf balls are easily cut and/or damaged if mis-hit. Golf balls produced with balata or balata-containing cover compositions therefore have a relatively short lifespan.

As a result of this negative property, balata and its synthetic substitutes, transpolyisoprene and transpolybutadiene, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

Ionomeric resins are polymers containing interchain ionic bonding. As a result of their toughness, durability and flight characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and more recently, by the Exxon Corporation (see U.S. Pat. No. 4,911,451) under the trademarks "Escor®" and the trade name "Iotek", have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or synthetic) rubbers. As stated, the softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties required for repetitive play.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated

carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Metal ions, such as sodium or zinc, are used to neutralize some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, while there are currently more than fifty (50) commercial grades of ionomers available both from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc., a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved impact resistance and carrying distance properties produced by the "hard" ionomeric resins, but also the playability (i.e., "spin", "feel", etc.) characteristics previously associated with the "soft" balata covers, properties which are still desired by the more skilled golfer.

Consequently, a number of two-piece (a solid resilient center or core with a molded cover) and three-piece (a liquid or solid center, elastomeric winding about the center, and a molded cover) golf balls have been produced by the present inventor and others to address these needs. The different types of materials utilized to formulate the cores, covers, etc. of these balls dramatically alters the balls' overall characteristics.

In addition, multi-layered covers containing one or more ionomer resins have also been formulated in an attempt to produce a golf ball having the overall distance, playability and durability characteristics desired. For example, this was addressed by Spalding & Evenflo Companies, Inc., the assignee of the present invention, in U.S. Pat. No. 4,431,193 where a multi-layered regular sized, golf ball is disclosed.

In the '193 patent, a multi-layer golf ball is produced by initially molding a first cover layer on a spherical core and then adding a second layer. The first layer is comprised of a hard, high flexural modulus resinous material such as type 1605 Surlyn® (now designated Surlyn® 8940). Type 1605 Surlyn® (Surlyn® 8940) is a sodium ion based low acid (less than or equal to 15 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 51,000 psi. An outer layer of a comparatively soft, low flexural modulus resinous material such as type 1855 Surlyn® (now designated Surlyn® 9020) is molded over the inner cover layer. Type 1855 Surlyn® (Surlyn® 9020) is a zinc ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '193 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a

gain in coefficient of restitution over the coefficient of restitution of the core. The increase in the coefficient of restitution provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides essentially no gain in the coefficient of restitution but provides for the advantageous "feel" and playing characteristics of a balata covered golf ball.

Unfortunately, however, while a ball of the '193 patent does exhibit enhanced playability characteristics with improved distance (i.e. enhanced C.O.R. values) over a number of other then known multi-layered balls, the ball suffers from poor cut resistance and relatively short distance (i.e. lower C.O.R. values) when compared to two-piece, single cover layer balls commercially available today. These undesirable properties make the ball produced in accordance with the '193 patent unacceptable by today's standards.

The present invention is directed to new multi-layer golf ball compositions which provide for enhanced coefficient of restitution (i.e, enhanced resilience or carrying distance) and/or durability properties when compared to the multi-layer balls found in the prior art, as well as improved outer cover layer softness and durability. As such, the playability characteristics (i.e., "feel", "click", "spin", etc.) are not diminished.

These and other objects and features of the invention will be apparent from the following summary and description of the invention, the drawings and from the claims.

SUMMARY OF THE INVENTION

The present invention is directed to improved multi-layer golf ball cover compositions and the resulting multi-layer golf balls produced using the improved compositions. The novel multi-layer golf ball covers of the present invention include a first or inner layer or ply of a high acid (greater than 16 weight percent acid) ionomer blend or, more preferably, a low acid (16 weight percent acid or less) ionomer blend and second or outer layer or ply comprised of a comparatively softer, low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane or polyester elastomer. The multi-layer golf balls of the invention can be of standard or enlarged size. Preferably, the inner layer or ply incudes a blend of low acid ionomers and has a Shore D hardness of 60 or greater and the outer cover layer comprised of polyurethane and has a Shore D hardness of about 45 (i.e., Shore C hardness of about 65).

It has been found that multi-layer golf balls having inner and outer cover layers exhibit higher C.O.R. values and have greater travel distance in comparison with balls made from a single cover layer. In addition, it has been found that use of a inner cover layer constructed of a blend of low acid (i.e., 16 weight percent acid or less) ionomer resins produces softer compression and higher spin rates than inner cover layers constructed of high acid ionomer resins. This is compounded by the fact that the softer polyurethane outer layer adds to the desirable "feel" and high spin rate while maintaining respectable resiliency. The soft outer layer allows the cover to deform more during impact and

increases the area of contact between the club face and the cover, thereby imparting more spin on the ball. As a result, the soft polyurethane cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability.

Consequently, the overall combination of inner and outer cover layers made from blends of low acid ionomer resins and polyurethane results in a standard size or oversized golf ball having enhanced resilience (improved travel distance) and durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the balls playability properties.

The combination of a low acid ionomer blend inner cover layer with a soft, relatively low modulus ionomer, polyurethane based elastomer outer cover layer provides for good overall coefficient of restitution (i.e., enhanced resilience) while at the same time demonstrating improved compression and spin. The outer cover layer generally contributes to a more desirable feel and spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Resilience (C.O.R.), along with additional factors such as club head speed, angle of trajectory and ball configuration (i.e., dimple pattern) generally determine the distance a ball will travel when hit. Since club head speed and the angle of trajectory are factors not easily controllable by a manufacturer, factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

The coefficient of restitution (C.O.R.) in solid core balls is a function of the composition of the molded core and of the cover. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings. Although both the core and the cover contribute to the coefficient of restitution, the present invention is directed to the enhanced coefficient of restitution (and thus travel distance) which is affected by the cover components.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and measuring the ball's incoming and outgoing velocity electronically. As mentioned above, the coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States Golf Association (U.S.G.A.). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial

velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Pat. No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests such as the "nine iron" spin rate test described below in the Examples.

Accordingly, the present invention is directed to an improved multi-layer cover which produces, upon molding each layer around a core (preferably a solid core) to formulate a multi-layer cover, a golf ball exhibiting enhanced distance (i.e., resilience) without adversely affecting, and in many instances, improving the ball's playability (hardness/softness) and/or durability (i.e., cut resistance, fatigue resistance, etc.) characteristics.

These and other objects and features of the invention will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional view of a golf ball embodying the invention illustrating a core **10** and a cover **12** consisting of an inner layer **14** and an outer layer **16** having dimples **18**; and

FIG. **2** is a diametrical cross-sectional view of a golf ball of the invention having a core **10** and a cover **12** made of an inner layer **14** and an outer layer **16** having dimple **18**.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to improved multi-layer golf balls, particularly a golf ball comprising a multi-layered cover **12** over a solid core **10**, and method for making same.

The multi-layered cover **12** comprises two layers: a first or inner layer or ply **14** and a second or outer layer or ply **16**. The inner layer **14** is comprised of a low acid (i.e. 16 weight percent acid or less) ionomer blend. Preferably, the inner layer is comprised of a blend of two or more low acid (i.e. 16 weight percent acid or less) ionomer resins neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

The low acid ionomers which may be suitable for use in formulating the inner layer compositions of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10–75%, preferably 30–70%) by the metal ions. Each of the low acid ionomer resins which may be included in the inner layer cover compositions of the invention contains 16% by weight or less of a carboxylic acid.

The inner layer compositions include the low acid ionomers such as those developed and sold by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or tradename "Iotek", or blends thereof.

The low acid ionomeric resins available from Exxon under the designation "Escor®" and or "Iotek", are somewhat similar to the low acid ionomeric resins available under the "Surlyn®" trademark. However, since the Escor®/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the "Surlyn®" resins are zinc, sodium, magnesium, etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the low acid ionomer blends extend the range of compression and spin rates beyond that previously obtainable. More preferably, it has been found that when two or more low acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further and at an enhanced spin rate than previously known multi-layered golf balls. Such an improvement is particularly noticeable in enlarged or oversized golf balls.

For example, the normal size, multi-layer golf ball taught in U.S. Pat. No. 4,650,193 does not incorporate blends of low acid ionomeric resins of the present invention in the inner cover layer. In addition, the multi-layered ball disclosed in the '193 patent suffers substantially in durability in comparison with the present invention.

Furthermore, as shown in the Examples, use of a inner layer formulated from blends of lower acid ionomers produces multi-layer golf balls having enhanced compression and spin rates. These are the properties desired by the more skilled golfer.

With respect to the outer layer **16** of the multi-layered cover of the present invention, the outer cover layer is comparatively softer than the low acid ionomer blend based inner layer. The softness provides for the enhanced feel and playability characteristics typically associated with balata or balata-blend balls. The outer layer or ply is comprised of a relatively soft, low modulus (about 1,000 psi to about 10,000 psi) and low acid (less than 16 weight percent acid) ionomer, ionomer blend or a non-ionomeric elastomer such as, but not limited to, a polyurethane, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, a poly-

urethane sold by BASF under the designation Baytec® or a polyester amide such as that marketed by Elf Atochem S.A. under the trademark Pebax®. The outer layer is fairly thin (i.e. from about 0.010 to about 0.070 in thickness, more desirably 0.03 to 0.06 inches in thickness for a 1.680 inch ball and 0.04 to 0.07 inches in thickness for a 1.72 inch ball), but thick enough to achieve desired playability characteristics while minimizing expense.

Preferably, the outer layer includes a blend of hard and soft (low acid) ionomer resins such as those described in U.S. Pat. Nos. 4,884,814 and 5,120,791, both incorporated herein by reference. Specifically, a desirable material for use in molding the outer layer comprises a blend of a high modulus (hard), low acid, ionomer with a low modulus (soft), low acid, ionomer to form a base ionomer mixture. A high modulus ionomer herein is one which measures from about 15,000 to about 70,000 psi as measured in accordance with ASTM method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240.

A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale.

The hard ionomer resins utilized to produce the outer cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium or lithium salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15–75 percent) neutralized.

The hard ionomeric resins are likely copolymers of ethylene and either acrylic and/or methacrylic acid, with copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

As discussed earlier herein, the hard ionomeric resins introduced under the designation Escor® and sold under the designation "Iotek" are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However, since the "Iotek" ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of poly(ethylene-methacrylic acid) some distinct differences in properties exist. As more specifically indicated in the data set forth below, the hard "Iotek" resins (i.e., the acrylic acid based hard ionomer resins) are the more preferred hard resins for use in formulating the outer layer blends for use in the present invention. In addition, various blends of "Iotek" and Surlyn® hard ionomeric resins, as well as other available ionomeric resins, may be utilized in the present invention in a similar manner.

Examples of commercially available hard ionomeric resins which may be used in the present invention in formulating the inner and outer cover blends include the hard sodium ionic copolymer sold under the trademark Surlyn®8940 and the hard zinc ionic copolymer sold under the trademark Surlyn®9910. Surlyn®8940 is a copolymer of ethylene with methacrylic acid and about 15 weight percent acid which is about 29 percent neutralized with sodium ions. This resin has an average melt flow index of about 2.8. Surlyn®9910 is a copolymer of ethylene and methacrylic acid with about 15 weight percent acid which is about 58 percent neutralized with zinc ions. The average melt flow index of Surlyn®9910 is about 0.7. The typical properties of Surlyn®9910 and 8940 are set forth below in Table 1:

TABLE 1

Typical Properties of Commercially Available Hard Surlyn ® Resins Suitable for Use in the Inner and Outer Layer Blends of the Present Invention

	ASTM D	8940	9910	8920	8528	9970	9730
Cation Type		Sodium	Zinc	Sodium	Sodium	Zinc	Zinc
Melt flow index, gms/10 min.	D-1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, g/cm^3	D-792	0.95	0.97	0.95	0.94	0.95	0.95
Hardness, Shore D	D-2240	66	44	66	60	62	63
Tensile Strength, (kpsi), MPa	D-638	(4.8) 33.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(4.1) 28.0
Elongation, %	D-638	470	290	350	450	460	460
Flexural Modulus, (kpsi) MPa	D-790	(51) 350	(48) 330	(55) 380	(32) 220	(28) 190	(30) 210
Tensile Impact (23° C.) KJ/m_2 (ft.-lbs./in^2)	D-1822S	1020 (485)	1020 (485)	865 (410)	1160 (550)	760 (360)	1240 (590)
Vicat Temperature, ° C.	D-1525	63	62	58	73	61	73

Examples of the more pertinent acrylic acid based hard ionomer resin suitable for use in the present inner and outer cover composition sold under the "Iotek" tradename by the Exxon Corporation include Iotek 4000, Iotek 4010, Iotek 8000, Iotek 8020 and Iotek 8030. The typical properties of these and other Iotek hard ionomers suited for use in formulating the inner and outer layer cover compositions are set forth below in Table 2:

TABLE 2

Typical Properties of Iotek Ionomers

	ASTM Method	Units	4000	4010	8000	8020	8030
Resin Properties							
Cation type			zinc	zinc	sodium	sodium	sodium
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6	2.8
Density	D-1505	kg/m^3	963	963	954	960	960
Melting Point	D-3417	° C.	90	90	90	87.5	87.5
Crystallization Point	D-3417	° C.	62	64	56	53	55
Vicat Softening Point	D-1525	° C.	62	63	61	64	67
% Weight Acrylic Acid			16		11		
% of Acid Groups cation neutralized			30		40		
Plaque Properties (3 mm thick, compression molded)							
Tensile at break	D-638	MPa	24	26	36	31.5	28
Yield point	D-638	MPa	none	none	21	21	23
Elongation at break	D-638	%	395	420	350	410	395
1% Secant modulus	D-638	MPa	160	160	300	350	390
Shore Hardness D	D-2240	—	55	55	61	58	59
Film Properties (50 micron film 2.2:1 Blow-up ratio)							
Tensile at Break							
MD	D-882	MPa	41	39	42	52	47.4
TD	D-882	MPa	37	38	38	38	40.5
Yield point							
MD	D-882	MPa	15	17	17	23	21.6
TD	D-882	MPa	14	15	15	21	20.7
Elongation at Break							
MD	D-882	%	310	270	260	295	305
TD	D-882	%	360	340	280	340	345
1% Secant modulus							
MD	D-882	MPa	210	215	390	380	380
TD	D-882	MPa	200	225	380	350	345
Dart Drop Impact	D-1709	g/micron	12.4	12.5	20.3		

	ASTM Method	Units	7010	7020	7030
Resin Properties					
Cation type			zinc	zinc	zinc
Melt Index	D-1238	g/10 min.	0.8	1.5	2.5
Density	D-1505	kg/m^3	960	960	960
Melting Point	D-3417	° C.	90	90	90
Crystallization Point	D-3417	° C.	—	—	—
Vicat Softening Point	D-1525	° C.	60	63	62.5
% Weight Acrylic Acid			—	—	—
% of Acid Groups Cation Neutralized			—	—	—
Plaque Properties (3 mm thick, compression molded)					
Tensile at break	D-638	MPa	38	38	38
Yield Point	D-638	MPa	none	none	none
Elongation at break	D-638	%	500	420	395
1% Secant modulus	D-638	MPa	—	—	—
Shore Hardness D	D-2240	—	57	55	55

Comparatively, soft ionomers are used in formulating the hard/soft blends of the inner and outer cover compositions. These ionomers include acrylic acid based soft ionomers. They are generally characterized as comprising sodium or zinc salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, acrylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably a zinc based ionomer made from an acrylic acid base polymer in an unsaturated monomer of the acrylate ester class. The soft (low modulus) ionomers have a hardness from about 20 to about 40 as measured on the Shore D scale and a flexural modulus from about 1,000 to about 10,000, as measured in accordance with ASTM method D-790.

Certain ethylene-acrylic acid based soft ionomer resins developed by the Exxon Corporation under the designation "Iotek 7520" (referred to experimentally by differences in neutralization and melt indexes as LDX 195, LDX 196, LDX 218 and LDX 219) may be combined with known hard ionomers such as those indicated above to produce the inner and outer cover layers. The combination produces higher C.O.R.s at equal or softer hardness, higher melt flow (which corresponds to improved, more efficient molding, i.e., fewer rejects) as well as significant cost savings versus the inner and outer layers of multi-layer balls produced by other known hard-soft ionomer blends as a result of the lower overall raw materials costs and improved yields.

While the exact chemical composition of the resins to be sold by Exxon under the designation Iotek 7520 is considered by Exxon to be confidential and proprietary information, Exxon's experimental product data sheet lists the following physical properties of the ethylene acrylic acid zinc ionomer developed by Exxon:

TABLE 3

Physical Properties of Iotek 7520

Property	ASTM Method	Units	Typical Value
Melt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m^3	0.962
Cation			Zinc
Melting Point	D-3417	° C.	66
Crystallization Point	D-3417	° C.	49
Vicat Softening Point	D-1525	° C.	42
Plaque Properties (2 mm thick Compression Molded Plaques)			
Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	None
Elongation at Break	D-638	%	760
1% Secant Modulus	D-638	MPa	22
Shore D Hardness	D-2240		32
Flexural Modulus	D-790	MPa	26
Zwick Rebond	ISO 4862	%	52
De Mattia Flex Resistance	D-430	Cycles	>5000

In addition, test data collected by the inventor indicates that Iotek 7520 resins have Shore D hardnesses of about 32 to 36 (per ASTM D-2240), melt flow indexes of 3±0.5 g/10 min (at 190° C. per ASTM D-1288), and a flexural modulus of about 2500–3500 psi (per ASTM D-790). Furthermore, testing by an independent testing laboratory by pyrolysis mass spectrometry indicates that Iotek 7520 resins are generally zinc salts of a terpolymer of ethylene, acrylic acid, and methyl acrylate.

Furthermore, the inventor has found that a newly developed grade of an acrylic acid based soft ionomer available from the Exxon Corporation under the designation Iotek 7510, is also effective, when combined with the hard ionomers indicated above in producing golf ball covers exhibiting higher C.O.R. values at equal or softer hardness than those produced by known hard-soft ionomer blends. In this regard, Iotek 7510 has the advantages (i.e. improved flow, higher C.O.R. values at equal hardness, increased clarity, etc.) produced by the Iotek 7520 resin when compared to the methacrylic acid base soft ionomers known in the art (such as the Surlyn 8625 and the Surlyn 8629 combinations disclosed in U.S. Pat. No. 4,884,814).

In addition, Iotek 7510, when compared to Iotek 7520, produces slightly higher C.O.R. valves at equal softness/hardness due to the Iotek 7510's higher hardness and neutralization. Similarly, Iotek 7510 produces better release properties (from the mold cavities) due to its slightly higher stiffness and lower flow rate than Iotek 7520. This is important in production where the soft covered balls tend to have lower yields caused by sticking in the molds and subsequent punched pin marks from the knockouts.

According to Exxon, Iotek 7510 is of similar chemical composition as Iotek 7520 (i.e. a zinc salt of a terpolymer of ethylene, acrylic acid, and methyl acrylate) but is more highly neutralized. Based upon FTIR analysis, Iotek 7520 is estimated to be about 30–40 wt.-% neutralized and Iotek 7510 is estimated to be about 40–60 wt.-% neutralized. The typical properties of Iotek 7510 in comparison of those of Iotek 7520 are set forth below:

TABLE 4

Physical Properties of Iotek 7510 in Comparison to Iotek 7520

	IOTEK 7520	IOTEK 7510
MI, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Melting Point, ° F.	151	149
Vicat Softening Point, ° F.	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

It has been determined that when hard/soft ionomer blends are used for the outer cover layer, good results are achieved when the relative combination is in a range of about 90 to about 10 percent hard ionomer and about 10 to about 90 percent soft ionomer. The results are improved by adjusting the range to about 75 to 25 percent hard ionomer and 25 to 75 percent soft ionomer. Even better results are noted at relative ranges of about 60 to 90 percent hard ionomer resin and about 40 to 60 percent soft ionomer resin.

Specific formulations which may be used in the cover composition are included in the examples set forth in U.S. Pat. Nos. 5,120,791 and 4,884,814. The present invention is in no way limited to those examples.

Moreover, in alternative embodiments, the outer cover layer formulation may also comprise a soft, low modulus

non-ionomeric thermoplastic elastomer including a polyester polyurethane such as B.F.Goodrich Company's Estane® polyester polyurethane X-4517. According to B.F.Goodrich, Estane® X-4517 has the following properties:

Properties of Estane ® X-4517	
Tensile	1430
100%	815
200%	1024
300%	1193
Elongation	641
Youngs Modulus	1826
Hardness A/D	88/39
Dayshore Rebound	59
Solubility in Water	Insoluble
Melt processing temperature	>350° F. (>177° C.)
Specific Gravity (H_2O = 1)	1.1–1.3

Other soft, relatively low modulus non-ionomeric thermoplastic elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced spin characteristics produced by the low acid ionomer resin compositions. These include, but are not limited to thermoplastic polyurethanes such as: Texin thermoplastic polyurethanes from Mobay Chemical Co. and the Pellethane thermoplastic polyurethanes from Dow Chemical Co.; Ionomer/rubber blends such as those in Spalding U.S. Pat. Nos. 4,986,545; 5,098,105 and 5,187,013; and, Hytrel polyester elastomers from DuPont and pebax polyesteramides from Elf Atochem S.A.

Similarly, a castable, thermosetting polyurethane produced by BASF under the trade designation Baytec® has also shown enhanced cover formulation properties. According to BASF, Baytec® (such as Baytec® RE 832), relates to a group of reactive elastomers having outstanding wear resistance, high mechanical strength, high elasticity and good resistance to weathering, moisture and chemicals. The Baytec® RE-832 system gives the following typical physical properties:

Property	ASTM Test Method	Unit	Value
Tear Strength Die C	D624	pli	180
Stress at			
100% Modulus	D412	psi	320
200% Modulus			460
300% Modulus			600
Ultimate Strength	D412	psi	900
Elongation at Break	D412	%	490
Taber Abrasion	D460, H-18	mg/1000 cycles	350

Component[1] Properties	Part A (Isocyanate)	Part B (Resin)
Viscosity @ 25° C., mPa · s	2500	2100
Density @ 25° C., g/cm	1.08	1.09
NCO, %	9.80	—
Hydroxyl Number, Mg KOH/g	—	88

[1]Component A is a modified diphenylmethane diisocyanate (mDI) prepolymer and component B is a polyether polyol blend.

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core) A comparatively softer outer layer is molded over the inner layer.

The conventional solid core is about 1.545 inches in diameter, although it can range from about 1.495 to about 1.575 inches. Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an α, β, ethylenically unsaturated carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include fillers such as small amounts of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the desired coefficient are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiators such as peroxides are admixed with the core composition so that on the application of heat and pressure, a complex curing cross-linking reaction takes place.

The inner cover layer which is molded over the core is about 0.100 inches to about 0.010 inches in thickness, preferably about 0.0375 inches thick. The outer cover layer is about 0.010 inches to about 0.050 inches in thickness, preferably 0.0300 inches thick. Together, the core, the inner cover layer and the outer cover layer combine to form a ball having a diameter of 1.680 inches or more, the minimum diameter permitted by the rules of the United States Golf Association and weighing about 1.620 ounces.

Additional materials may be added to the cover compositions (both inner and outer cover layer) of the present invention including dyes (for example, Ultramarine Blue sold by Whitaker, Clark and Daniels of South Plainsfield, N.J.) (see U.S. Pat. No. 4,679,795); pigments such as titanium dioxide, zinc oxide, barium sulfate and zinc sulfate; and UV absorbers; antioxidants; antistatic agents; and stabilizers. Further, the cover compositions of the present invention may also contain softening agents, such as plasticizers, processing aids, etc. and reinforcing material such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers are not impaired.

The various cover composition layers of the present invention may be produced according to conventional melt blending procedures. In the case of the outer cover layer, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the

desired additives in a Banbury mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the low acid ionomer resin compositions used to produce the inner cover layer.

The golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the inner cover layer about wound or solid molded cores to produce an intermediate golf ball having a diameter of about 1.50 to 1.67 inches, preferably about 1.620 inches. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.680 inches or more. Although either solid cores or wound cores can be used in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound cores.

In compression molding, the inner cover composition is formed via injection at about 380° F. to about 450° F. into smooth surfaced hemispherical shells which are then positioned around the core in a mold having the desired inner cover thickness and subjected to compression molding at 200° to 300° F. for about 2 to 10 minutes, followed by cooling at 50° to 70° F. for about 2 to 7 minutes to fuse the shells together to form a unitary intermediate ball. In addition, the intermediate balls may be produced by injection molding wherein the inner cover layer is injected directly around the core placed at the center of an intermediate ball mold for a period of time in a mold temperature of from 50° F. to about 100° F. Subsequently, the outer cover layer is molded about the core and the inner layer by similar compression or injection molding techniques to form a dimpled golf ball of a diameter of 1.680 inches or more.

After molding, the golf balls produced may undergo various further processing steps such as buffing, painting and marking as disclosed in U.S. Pat. No. 4,911,451.

The resulting golf ball produced from the low acid ionomer resin inner layer and the relatively softer, low flexural modulus outer layer provide for an improved multilayer golf ball which provides for desirable coefficient of restitution, compression, spin and durability properties while at the same time offering the feel characteristics associated with soft balata and balata-like covers of the prior art.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

EXAMPLE 1

Several intermediate balls (cores plus inner cover layers) were prepared in accordance with conventional molding procedures described above. The inner cover compositions were molded around 1.545 inch diameter cores weighing 36.5 grams such that the inner cover had a wall thickness of about 0.0675 inches, with the overall ball measuring about 1.680 inches in diameter.

The cores utilized in the examples were comprised of the following ingredients: high cis-polybutadiene, zinc diacrylate, zinc oxide, zinc stearate, peroxide, calcium carbonate, etc. The molded cores exhibited Riehle compressions of about 60 and C.O.R. values of about 0.800. A representative formulation of the molded cores is set forth below:

MATERIAL	WEIGHT
BR-1220 (high cis-polybutadiene)	70.70
Taktene 220 (high cis-polybutadiene)	29.30
React Rite ZDA (zinc diacrylate)	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash (20–40 Mesh)	20.15
Blue Masterbatch	.012
Luperco 231XL or Trigonox 29/40	.89
Papi 94	.50

[1]Blue Masterbatch consists of unknown compositions used only for internal identification purposes and has no effect on physical properties.

The inner cover compositions designated herein as compositions A–E utilized to formulate the intermediate balls are set forth in Table 7 below. The resulting molded intermediate balls were tested to determine the individual compression (Riehle), C.O.R., Shore C hardness, spin rate and cut resistance properties. These results are also set forth in Table 7 below.

The data of these examples are the average of twelve intermediate balls produced for each example. The properties were measured according to the following parameters:

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air canon at a velocity of 125 feet per second against a steel plate positioned 12 feet from the muzzle of the canon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give a coefficient of restitution.

Shore hardness was measured in accordance with ASTM test 2240.

Cut resistance was measured in accordance with the following procedure: A golf ball is fired at 135 feet per second against the leading edge of a pitching wedge wherein the leading edge radius is 1/32 inch, the loft angle is 51 degrees, the sole radius is 2.5 inches and the bounce angle is 7 degrees.

The cut resistance of the balls tested herein was evaluated on a scale of 1 to 5. The number 1 represents a cut that extends completely through the cover to the core. A 2 represents a cut that does not extend completely through the cover but that does break the surface. A 3 does not break the surface of the cover but does leave a permanent dent. A 4 leaves only a slight crease which is permanent but not as severe as 3. A 5 represents virtually no visible indentation or damage of any sort.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9 iron wherein the club head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110 to 115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

Initial velocity is the velocity of a ball when struck at a hammer speed of 143.8 feet per second in accordance with a test as prescribed by the U.S.G.A.

As will be noted, compositions A, B and C include high acid ionomeric resins (16% or more acid), with composition B further including zinc stearate. Composition D represents the inner layer (i.e. Surlyn 1605) used in U.S. Pat. No. 4,431,193. Composition E provides a hard, low acid ionomeric resin blend.

The purpose behind producing and testing the balls of Table 5 was to provide a subsequent comparison in properties with the multi-layer golf balls of the present invention.

TABLE 5

Molded Intermediate Golf Balls	A	B	C	D	E
Ingredients of Inner Cover Compositions					
Iotek 959	50	50	—	—	—
Iotek 960	50	50	—	—	—
Zinc Stearate	—	50	—	—	—
Surlyn 8162	—	—	75	—	—
Surlyn 8422	—	—	25	—	—
Surlyn 1605	—	—	—	100	—
Iotek 7030	—	—	—	—	50
Iotek 8000	—	—	—	—	50
Properties of Molded Intermediate Balls					
Compression	58	58	60	63	62
C.O.R.	.811	.810	.807	.793	.801
Shore C Hardness	98	98	97	96	96
Spin Rate (R.P.M.)	7,367	6,250	7,903	8,337	7,956
Cut Resistance	4–5	4–5	4–5	4–5	4–5

As shown in Table 5 above, the high acid ionomer resin inner cover layer (molded intermediate balls A–C) have lower spin rates and exhibit higher resiliency characteristics than the low acid ionomer resin based inner cover layers of balls D and E.

Multi-layer balls in accordance with the present invention were then prepared. Specifically, the inner cover compositions used to produce intermediate golf balls from Table 5 were molded over the solid cores to a thickness of about 0.0375 inches, thus forming the inner layer. The diameter of the solid core with the inner layer measured about 1.620 inches. Alternatively, the intermediate golf balls of Table 5 were ground down using a centerless grinding machine to a size of 1.620 inches in diameter to produce an inner cover layer of 0.0375 inches.

The size of 1.620 inches was determined after attempting to mold the outer cover layer to various sizes (1.600", 1.610", 1.620", 1.630" and 1.640") of intermediate (core plus inner layer) balls. It was determined that 1.620" was about the largest "intermediate" ball (i.e., core plus inner layer) which could be easily molded over with the soft outer

layer materials of choice. The goal herein was to use as thin an outer layer as necessary to achieve the desired playability characteristics while minimizing the cost of the more expensive outer materials. However, with a larger diameter final golf ball and/or if the cover is compression molded, a thinner cover becomes feasible.

With the above in mind, an outer cover layer composition was blended together in accordance with conventional blending techniques. The outer layer composition used for this portion of the example is a relatively soft cover composition such as those listed in U.S. Pat. No. 5,120,791. An example of such a soft cover composition is a 45% soft/55% hard low acid ionomer blend designated by the inventor as "TE-90". The composition of TE-90 is set forth as follows:

Outer Cover Layer Composition TE-90	
Iotek 8000	22.7 weight %
Iotek 7030	22.7 weight %
Iotek 7520	45.0 weight %
White MB[1]	9.6 weight %

[1]White MB consists of about 23.77 weight percent TiO_2; 0.22 weight percent Uvitex OB, 0.03 weight percent Santonox R, 0.05 weight percent Ultramarine blue and 75.85 weight percent Iotek 7030.

The above outer layer composition was molded around each of the 1.620 diameter intermediate balls comprising a core plus one of compositions A–D, respectively. In addition, for comparison purposes, Surlyn® 1855 (new Surlyn® 9020), the cover composition of the '193 patent, was molded about the inner layer of composition D (the intermediate ball representative of the '193 patent). The outer layer TE-90 was molded to a thickness of approximately 0.030 inches to produce a golf ball of approximately 1.680 inches in diameter. The resulting balls (a dozen balls for each example) were tested and the various properties thereof are set forth in Table 6A as follows:

TABLE 6A

Finished Balls	1	2	3	4	5
Ingredients:					
Inner Cover Composition	A	B	C	D	D
Outer Cover Composition	TE-90	TE-90	TE-90	TE-90	Surlyn ® 9020
Properties of Molded Finished Balls:					
Compression	63	63	69	70	61
C.O.R.	.784	.778	.780	.770	.757
Shore C Hardness	88	88	88	88	89
Spin (R.P.M.)	8,825	8,854	8,814	8,990	8,846
Cut Resistance	3–4	3–4	3–4	3–4	1–2

As it will be noted in finished balls 1–4, by creating a multi-layer cover utilizing the high acid ionomer resins in the inner cover layer and the hard/soft low acid ionomer resins in the outer cover layer, higher compression and increased spin rates are noted over the single layer covers of Table 5. In addition, both the C.O.R. and the Shore C hardness are reduced over the respective single layer covers

of Table 5. This was once again particularly true with respect to the multi-layered balls containing the high acid ionomer resin in the inner layer (i.e. finished balls 1–4). In addition, with the exception of prior art ball 5 (i.e. the '193 patent), resistance to cutting remains good but is slightly decreased. As noted above, the prior art ball of the '193 patent suffers substantially in durability (as well as in resiliency) in comparison to the balls of the invention.

Furthermore, it is also noted that the use of the high acid ionomer resins as the inner cover material produces a substantial increase in the finished balls overall distance properties. In this regard, the high acid ionomer resin inner covers of balls 1–3 produce an increase of approximately 10 points in C.O.R. over the low acid ionomer resin inner covers of balls 4 and about a 25 point increase over the prior art balls 5. Since an increase in 3 to 6 points in C.O.R. results in an average increase of about 1 yard in distance, such an improvement is deemed to be significant.

Several other outer layer formulations were prepared and tested by molding them around the core and inner cover layer combination to form balls each having a diameter of about 1.68 inches. First, B.F.Goodrich Estane® X-4517 polyester polyurethane was molded about the core molded with inner layer cover formulation A. DuPont Surlyn® 9020 was molded about the core which was already molded with inner layer D. Similar properties tests were conducted on these golf balls and the results are set forth in Table 6B below:

TABLE 6B

	Finish Balls	
	6	7
Ingredients:		
Inner Cover Layer Composition	A	D
Outer Cover Layer Composition	Estane ® 4517	Surlyn ® 9020
Properties of Molded Finished Balls:		
Compression	67	61
C.O.R.	.774	.757
Shore C Hardness	74	89

TABLE 6B-continued

	Finish Balls	
	6	7
Spin (R.P.M.)	10,061	8,846
Cut Resistance	3–4	1–2

The ball comprising inner layer formulation D and Surlyn® 9020 identifies the ball in the Nesbitt U.S. Pat. No. 4,431,193. As is noted, the example provides for relatively high softness and spin rate though it suffers from poor cut resistance and low C.O.R. This ball is unacceptable by today's standards.

As for the Estane® X-4517 polyester polyurethane, a significant increase in spin rate over the TE-90 cover is noted along with an increased compression. However, the C.O.R. and Shore C values are reduced, while the cut resistance remains the same. Furthermore, both the Estane® X-4517 polyester polyurethane and the Surlyn® 9020 were relatively difficult to mold in such thin sections.

EXAMPLE 2

In order to analyze the change in characteristics produced by multi-layer golf balls (standard size) having inner cover layers comprised of ionomer resin blends of different acid levels, a series of experiments were run. Specifically, 14 tests were performed, varying the type of core, inner cover layer and outer cover layer. The results are shown below:

TABLE 7

Sample #	CORE	INNER LAYER	THICKNESS	COMP/ COR	OUTER COVER	THICKNESS	COMP (Rhiele)	COR	SHORE D	SPIN
8	1042 YELLOW	NONE	—	SEE BELOW	TOP GRADE	0.055"	61	.800	68	7331
9	1042 YELLOW	NONE	—	SEE BELOW	959/960	0.055"	56	.808	73	6516
10	SPECIAL 1.47"	959/960	0.050"	65/.805	959/960	0.055"	48	.830	73	6258
11	1042 YELLOW	NONE	—	SEE BELOW	SD 90	0.055"	62	.792	63	8421
12	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	SD 90	0.055"	55	.811	63	8265
13	SPECIAL 1.47"	959/960	0.050"	65/.805	SD 90	0.055"	53	.813	63	8254
14	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	TOP GRADE	0.055"	51	.819	68	7390
15	1042 YELLOW	NONE	—	SEE BELOW	Z-BALATA	0.055"	67	.782	55	9479
16	SPECIAL 1.47"	959/960	0.050"	65/.805	Z-BALATA	0.055"	61	.800	55	9026
17	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	Z-BALATA	0.055"	60	.798	55	9262

1042 YELLOW > COMP = 72, COR = .780
SPECIAL 1.47" CORE >COMP = 67, COR = .782

In this regard, "Top Grade" or "TG" is a low acid inner cover ionomer resin blend comprising of 70.6% Iotek 8000, 19.9% Iotek 7010 and 9.6% white masterbatch. "959/960" is a 50/50 wt/wt blend of Iotek 959/960. In this regard, Escor® or Iotek 959 is a sodium ion neutralized ethylene-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

PROPERTY	ESCOR ® (IOTEK) 959	ESCOR ® (IOTEK) 960
Melt Index g/10 min	2.0	1.8

-continued

PROPERTY	ESCOR ® (IOTEK) 959	ESCOR ® (IOTEK) 960
Cation	Sodium	Zinc
Melting Point, ° F.	172	174
Vicat Softening Point, ° F.	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, the low acid ionomer formulation for "SD 90" and "Z-Balata" are set forth below:

SD Cover	ZB Cover
17.2% Surlyn 8320	19% Iotek 8000
7.5% Surlyn 8120	19% Iotek 7030
49% Surlyn 9910	52.5% Iotek 7520
16.4% Surlyn 8940	9.5% white MB
9.7% white MB	

The data clearly indicates that higher C.O.R. and hence increase travel distance can be obtained by using multi-layered covered balls versus balls covered with single layers. However, some sacrifices in compression and spin are also noted. Further, as shown in comparing Example Nos. 12 vs. 13, Example Nos. 17 vs. 16, etc., use of lower acid level inner cover layers and relatively soft outer cover layers (i.e., 50 wt. % or more soft ionomer) produces softer compression and higher spin rates than the golf balls comprised of high acid inner cover layers. Consequently, use of blends of low acid ionomer resins to produce the inner layer of a multi-layer covered golf ball, produces not only enhanced travel distance but also enhanced compression and spin properties.

EXAMPLE 3

Multi-layer oversized golf balls were produced utilizing different ionomer resin blends as the inner cover layer (i.e., core plus inner cover layer is defined as "mantel"). The "ball data" of the oversized multi-layer golf balls in comparison with production samples of "Top-Flite® XL" and "Top-Flite® Z-Balata" is set forth below.

TABLE 8

	18	19	20	21 Top-Flite ® XL	22 Top-Flite ® Z-Balata 90
Core Data					
Size	1.43	1.43	1.43	1.545	1.545
COR	.787	.787	.787	—	—
Mantel Data					
Material	TG	TG	TG	—	—
Size	.161	1.61	1.61	—	—
Thickness	.090	.090	.090	—	—
Shore D	68	68	68	—	—
Compression	57	57	57	—	—
COR	.815	.815	.815	—	—
Ball Data					
Cover	TG	ZB	SD	TG	ZB
Size	1.725	1.723	1.726	1.681	1.683
Weight	45.2	45.1	45.2	45.3	45.5
Shore D	68	56	63	68	56
Compression	45	55	49	53	77
COR	.820	.800	.810	.809	.797
Spin	7230	9268	8397	7133	9287

The results indicate that use of multi-layer covers enhances C.O.R. and travel distance. Further, the data shows that use of a blend of low acid ionomer resins (i.e., "Top Grade") to form the inner cover layer in combination with a soft outer cover ("ZB" or "SD") produces enhanced spin and compression characteristics. The overall combination results in a relatively optimal golf ball with respect to characteristics of travel distances, spin and durability.

EXAMPLE 4

Castable Polyurethane Covered Multi-layer Balls

A limited number of samples were made using BASF Baytec® RE232 polyurethane as a cover material over four different types of mantle cores. Controls included Z-Balata 100s along with the same mantle cores used for the polyurethane samples covered with Z-Balata cover stock. Mantle cores were made up of 82 and 58 compression cores covered with Iotek 8030/7030.

Castable PU Molding Process

Materials used:

Baytec® RE832, mix ratio 9 parts A/12 parts B

1—1.57" i.d. smooth cavity

2—1.68" i.d. dimpled cavities

1—2" hose clamp

1—bench vise or large C-clamp

(The smooth and dimpled cavities are the same O.D.)

The mantle core is 1.57" and fits snugly in the 1.57" cavity. The hose clamp is attached to the 1.57" cavity and a mantle core is placed in inside. Urethane is mixed and poured into one of the dimpled cavities and the two halves are placed together and clamped, forcing out excess material and forming half the cover. The hose clamp is used to keep the two mold halves aligned during curing. When the cover material is set up enough (about 5 minutes), the two halves are separated and the 1.57" mold is replaced with the other 1.68" mold and the process is repeated. Both halves of the cover are now cast and the entire assemble is placed in an 125 F. oven for 1 hour after which it can be opened and the ball removed.

All samples were finished using normal production equipment and procedures. The properties of the finished balls are set forth below:

TABLE 9

	23	23	24	25	26	27	28	29
CORE DATA								
Size	1.47"	1.47"	1.47"	1.47"	1.47"	1.47"	1.47"	1.47"
Weight	32.2	32	32.2	32	37.7	32.2	32	32.2
Comp	82	58	82	58	85	82	58	82
COR	768	772	768	772	794	768	772	768
MANTLE DATA	Iotek	Iotek	Iotek	Iotek		Iotek	Iotek	Iotek
Material	8030/7030	8030/7030	8030/7030	8030/7030	None	8030/7030	8030/7030	8030/7030
Weight	37.8	38.1	37.9	38.1		37.8	38.1	37.9
Size	1.58"	1.57"	1.57"	1.57"		1.57"	1.57"	1.57"
Comp	70	48	69	48		70	48	69
COR	781	785	786	788		781	785	786
BALL DATA								
Cover Material	Baytec RE832	Baytec RE832	Baytec RE832	Baytec RE832	Z-Balata	Z-Balata	Z-Balata	Z-Balata
Weight	45.4	45.5	45.5	45.2	45.3	44.8	45	
Comp	75	64	73	60	80	66	50	65
COR	771	763	770	761	792	775	774	778
Shore C	65	65	65	65	84	84	84	84
Spin (rpm)	9560	8789	9285	8760	8796	8702	9072	8643
Cut (1-good, 4-poor)	2	2	2	1.5	2	2	2	2
Scuff (1-good, 4-poor)	1.5	1.5	1.5	1.5	2	3	3	3

Table 9 contains the construction details and test results. Multilayer balls with the thermoset urethane covers (Examples 23–25) were softer in compression and similar in COR to the multi-layer balls with the Z-Balata cover (Examples 27–29) shore C was much lower for the urethane balls and they were more resistant to scuff than any of the Z-Balata covered balls. Guillotine cut resistance was about the same. Spin rate comparison shows that the urethane samples are better than the Z-Balata covered balls.

Test results indicate that a very good multi-layer ball can be made using castable polyurethane cover material. Further, advantages include the molding very thin covers, molding over very soft compression core/mantle, and low cost tooling.

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon reading and understanding the proceeding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

I claim:

1. A golf ball comprising:

a core;

an inner cover layer having a Shore D hardness of 60 or more molded on said core, said inner cover layer having a thickness of 0.100 to 0.010 inches, said inner cover layer comprising a blend of two or more low acid ionomer resins containing no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid; and

an outer cover layer having a Shore D hardness of 64 or less molded on said inner cover layer, said outer cover layer having a thickness of 0.010 to 0.070 inches, and said outer cover layer comprising a relatively soft polyurethane material.

2. The golf ball according to claim **1**, wherein said golf ball has an overall diameter of 1.680 inches or more.

3. The golf ball according to claim **1**, wherein said inner cover layer has a thickness of about 0.050 inches, said outer cover layer has a thickness of about 0.055 inches, and said golf ball has an overall diameter of 1.680 inches or more.

4. A multi-layer golf ball comprising:

a spherical core;

an inner cover layer having Shore D hardness of about 60 or more molded over said spherical core, said inner cover layer comprising an ionomeric resin including no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi; and

an outer cover layer having a Shore D hardness of about 64 or less disposed about said inner cover layer and defining a plurality of dimples to form a multi-layer golf ball, said outer cover layer comprising polyurethane based material.

5. A golf ball according to claim **4**, wherein said inner cover layer has a thickness of about 0.100 to about 0.010 inches and said outer cover layer has a thickness of about 0.010 to about 0.070 inches, said golf ball having an overall diameter of 1.680 inches or more.

6. A golf ball according to claim **4** wherein said inner cover layer has a thickness of about 0.050 inches and said outer cover layer has a thickness of about 0.055 inches, said golf ball having an overall diameter of 1.680 inches or more.

7. A multi-layer golf ball comprising:

a spherical core;

an inner cover layer molded over said spherical core to form a spherical intermediate ball, said inner cover layer having a Shore D hardness of at least 60, said inner cover layer comprising an ionomeric resin having no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi; and

a dimpled outer cover layer molded over said spherical intermediate ball to form a multi-layer golf ball, said outer cover having a Shore D hardness of 64 or less, said outer layer comprising a polyurethane, said outer cover layer having a modulus in a range of about 1,000 to about 30,000 psi.

8. The multi-layer golf ball of claim **7** wherein the Shore D hardness of said outer cover layer is less than the Shore D hardness of said inner cover layer.

* * * * *

Exhibit B

US006503156B1

(12) United States Patent
Sullivan

(10) Patent No.: **US 6,503,156 B1**
(45) Date of Patent: ***Jan. 7, 2003**

(54) **GOLF BALL HAVING MULTI-LAYER COVER WITH UNIQUE OUTER COVER CHARACTERISTICS**

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(73) Assignee: **Spalding Sports Worldwide, Inc.**, Chicopee, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/873,642**

(22) Filed: **Jun. 4, 2001**

Related U.S. Application Data

(63) Continuation of application No. 09/776,878, filed on Feb. 2, 2001, which is a continuation of application No. 09/470,196, filed on Dec. 21, 1999, now Pat. No. 6,210,393, which is a continuation of application No. 08/870,585, filed on Jun. 6, 1997, now abandoned, which is a continuation of application No. 08/556,237, filed on Nov. 9, 1995, now abandoned, which is a continuation-in-part of application No. 08/070,510, filed on Jun. 1, 1993, now abandoned.

(51) **Int. Cl.**^{7} **A63B 37/12**
(52) **U.S. Cl.** **473/374**
(58) **Field of Search** 473/378, 377, 473/376, 372, 371, 370, 373, 374

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,741,480	A	4/1956	Smith
2,973,800	A	3/1961	Muccino
3,053,539	A	9/1962	Piechowski
3,264,272	A	8/1966	Rees
3,313,545	A	4/1967	Bartsch
3,372,123	A	3/1968	Brice
3,384,612	A	5/1968	Brandt et al.
3,395,109	A	7/1968	Molitor et al.
3,458,205	A	7/1969	Smith et al.
3,502,338	A	3/1970	Cox
3,534,965	A	10/1970	Harrison et al.
3,572,721	A	3/1971	Harrison et al.

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

CA	2137841	6/1995
EP	0589647	3/1994
EP	0630665	12/1994
EP	0637459	2/1995
GB	494031	10/1938

(List continued on next page.)

OTHER PUBLICATIONS

Bayer Corporation, "Engineering Polymers Properties Guide Thermoplastics and Polyurethanes," brochure, pp. 2–7, 28–29.

A Properties Guide, "Engineering Polymers Thermoplastics and Thermosets," Miles Inc., 1–23 (1994).

Polyurethane Handbook, "Chemistry–Raw Materials–Processing Applications–Proeprties," edited by Oertel et al., Hanser/Gardner Publications, Inc., 101, 102 (1994).

(List continued on next page.)

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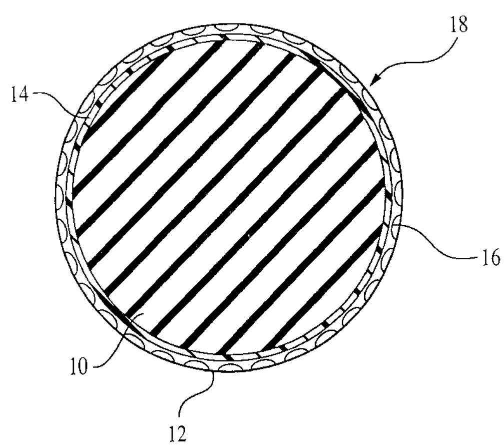
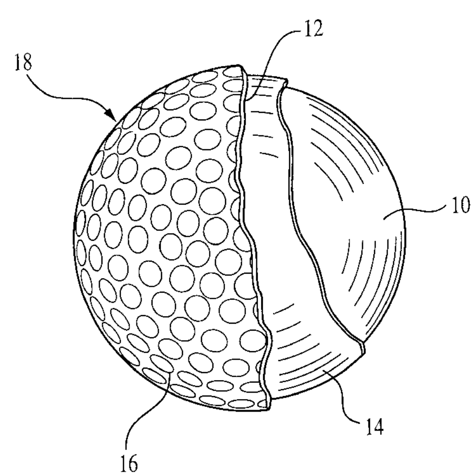
(57) **ABSTRACT**

The present invention is directed to an improved multi-layer golf ball comprising a core, an inner cover layer and an outer cover layer. The inner cover layer is comprised of a low acid ionomer blend which may or may not include a filler such as zinc-stearate. The outer cover layer is comprised of a soft, non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane, polyester or polyesteramide. The resulting multi-layered golf ball of the present invention provides for enhanced distance without sacrificing playability or durability when compared to known multi-layer golf balls.

11 Claims, 1 Drawing Sheet





U.S. PATENT DOCUMENTS

3,883,145 A 5/1975 Cox et al.
3,979,126 A 9/1976 Dusbiber
3,989,568 A 11/1976 Isaac
4,076,255 A 2/1978 Moore et al.
4,085,937 A 4/1978 Schenk
4,123,061 A 10/1978 Dusbiber
4,190,711 A 2/1980 Zdrahala et al.
4,218,543 A 8/1980 Weber et al.
4,248,432 A 2/1981 Hewitt et al.
4,272,079 A 6/1981 Nakade et al.
4,274,637 A 6/1981 Molitor
4,337,946 A 7/1982 Saito et al.
4,431,193 A * 2/1984 Nesbitt 473/373
4,442,282 A 4/1984 Kolycheck
4,570,937 A 2/1986 Yamada
4,582,887 A 4/1986 Dominguez et al.
4,590,219 A 5/1986 Nissen et al.
4,607,090 A 8/1986 Dominguez
4,650,193 A 3/1987 Molitor et al.
4,674,751 A 6/1987 Molitor et al.
4,679,795 A 7/1987 Melvin et al.
4,688,801 A 8/1987 Reiter
4,690,981 A 9/1987 Statz
4,695,055 A 9/1987 Newcomb et al.
4,714,253 A 12/1987 Nakahara et al.
4,762,322 A 8/1988 Molitor et al.
4,798,386 A 1/1989 Berard
4,848,770 A 7/1989 Shama
4,852,884 A 8/1989 Sullivan
4,858,923 A 8/1989 Gobush et al.
4,858,924 A 8/1989 Saito et al.
4,878,674 A 11/1989 Newcomb et al.
4,884,814 A 12/1989 Sullivan
4,911,451 A 3/1990 Sullivan et al.
4,919,434 A 4/1990 Saito
4,957,297 A 9/1990 Newcomb et al.
4,979,746 A 12/1990 Gentiluomo
4,984,804 A 1/1991 Yamada et al.
4,986,545 A 1/1991 Sullivan
5,002,281 A 3/1991 Nakahara et al.
5,006,297 A 4/1991 Brown et al.
5,019,319 A 5/1991 Nakamura et al.
5,026,067 A 6/1991 Gentiluomo
5,035,425 A 7/1991 Edwards
5,045,591 A 9/1991 Meyer et al.
5,048,838 A 9/1991 Chikaraishi et al.
5,068,151 A * 11/1991 Nakamura 473/374
5,072,944 A 12/1991 Nakahara et al.
5,096,201 A 3/1992 Egashira et al.
5,098,105 A 3/1992 Sullivan
5,104,126 A 4/1992 Gentiluomo
5,120,791 A 6/1992 Sullivan
5,142,835 A 9/1992 Mrocca
5,150,906 A 9/1992 Molitor et al.
5,156,405 A 10/1992 Kiotaoh et al.
5,184,828 A 2/1993 Kim et al.
5,187,013 A 2/1993 Sullivan
5,197,740 A 3/1993 Pocklington et al.
5,219,973 A 6/1993 Slack et al.
5,222,739 A 6/1993 Horiuchi et al.
5,244,969 A 9/1993 Yamada
5,253,871 A 10/1993 Viollaz
5,273,286 A 12/1993 Sun
5,273,287 A 12/1993 Molitor et al.
5,274,041 A 12/1993 Yamada
5,281,651 A 1/1994 Arjunan et al.
5,300,334 A 4/1994 Niederst et al.
5,304,608 A 4/1994 Yabuki et al.
5,306,760 A 4/1994 Sullivan
5,312,857 A 5/1994 Sullivan
5,314,187 A * 5/1994 Proudfit 473/373
5,324,783 A 6/1994 Sullivan
5,330,837 A 7/1994 Sullivan
5,334,673 A 8/1994 Wu
5,338,610 A 8/1994 Sullivan
5,368,304 A 11/1994 Sullivan et al.
5,368,806 A 11/1994 Harasin et al.
5,387,750 A 2/1995 Chiang
5,403,010 A 4/1995 Yabuki et al.
5,439,227 A 8/1995 Egashira et al.
5,480,155 A 1/1996 Molitor et al.
5,482,285 A 1/1996 Yabuki et al.
5,484,870 A 1/1996 Wu
5,490,673 A 2/1996 Hiraoka
5,490,674 A 2/1996 Hamada et al.
5,492,972 A 2/1996 Stefani
5,553,852 A 9/1996 Higuchi et al.
5,586,950 A 12/1996 Endo
5,628,699 A 5/1997 Maruko et al.
5,668,239 A 9/1997 Nodelman et al.
5,674,137 A 10/1997 Maruko et al.
5,688,191 A 11/1997 Cavallaro et al.
5,692,974 A 12/1997 Wu et al.
5,730,665 A 3/1998 Shimosaka et al.
5,733,206 A 3/1998 Nesbitt et al.
5,733,207 A 3/1998 Sullivan et al.
5,733,428 A 3/1998 Calabria et al.
5,739,247 A 4/1998 Lesko et al.
5,739,253 A 4/1998 Nodelman et al.
5,750,580 A 5/1998 Mayer et al.
5,759,676 A 6/1998 Cavallaro et al.
5,779,561 A 7/1998 Sullivan et al.
5,779,562 A 7/1998 Melvin et al.
5,779,563 A 7/1998 Yamagishi et al.
5,783,293 A 7/1998 Lammi
5,792,008 A 8/1998 Kkakiuchi et al.
5,797,808 A 8/1998 Hayashi et al.
5,800,284 A 9/1998 Sullivan et al.
5,803,831 A 9/1998 Sullivan et al.
5,810,678 A 9/1998 Cavallaro et al.
5,813,923 A 9/1998 Cavallaro et al.
5,816,937 A 10/1998 Shimosaka et al.
5,820,488 A 10/1998 Sullivan et al.
5,820,489 A 10/1998 Sullivan et al.
5,820,491 A 10/1998 Hatch et al.
5,827,167 A 10/1998 Dougan et al.
5,830,087 A 11/1998 Sullvan et al.
5,833,553 A 11/1998 Sullivan et al.
5,833,554 A 11/1998 Sullivan et al.
5,836,833 A 11/1998 Shimosaka et al.
5,849,168 A 12/1998 Lutz
5,856,388 A 1/1999 Harris et al.
5,863,264 A 1/1999 Yamagishi et al.
5,873,796 A 2/1999 Cavallaro et al.
5,885,172 A 3/1999 Hebert et al.
5,888,437 A 3/1999 Calabria et al.
5,891,973 A 4/1999 Sullivan et al.
5,897,884 A 4/1999 Calabria et al.
5,899,822 A 5/1999 Yamagishi et al.
5,902,192 A 5/1999 Kashiwagi et al.
5,908,358 A 6/1999 Wu
5,919,100 A 7/1999 Boehm et al.
5,919,862 A 7/1999 Rajagopalan
5,922,252 A 7/1999 Stanton et al.
5,929,189 A 7/1999 Ichikawa et al.
5,935,021 A 8/1999 Kashiwagi et al.
5,947,842 A 9/1999 Cavallaro et al.
5,947,843 A 9/1999 Calabria et al.
5,959,059 A 9/1999 Vedula et al.

5,976,035	A		11/1999	Umezawa et al.
5,984,807	A		11/1999	Wai et al.
6,210,293	B1	*	4/2001	Sullivan 473/374

FOREIGN PATENT DOCUMENTS

GB	2245580	1/1992
GB	2248067	3/1992
GB	2264302	11/1992
GB	2291811	2/1996
GB	2291812	2/1996

OTHER PUBLICATIONS

A General Reference Manual, "The Chemistry of Polyurethane Coatings," Mobay Corporation, 1–16 (1988).

Product Announcement, "New Polyurea System Offering Rapid Mold Times and Excellent Thermal Stability for Automotive Fascias Is Introducted by Movay," PRNewswire, Mar. 1, 1998.

Cytec Industries, Inc., "TMXDI®(META) Aliphatic Isocyanates," brochure, pp. 2–11, 9/94.

Bayer Corporation, "Engineering Polymers RIM and Parrt Mold Design," brochure, pp. 1–85, 5/95.

Translated Claims for JP 1,795,357 publ. Jan. 19, 1993.

DuPont NUCLREL 035 Resin, DuPont Company, Wilmington, DE 1989 (no date).

ESCOR Acid Terpolymers, EXXON Chemical Co.

Translated Claims for JP 1,771,941 publ. Aug. 6, 1992.

* cited by examiner

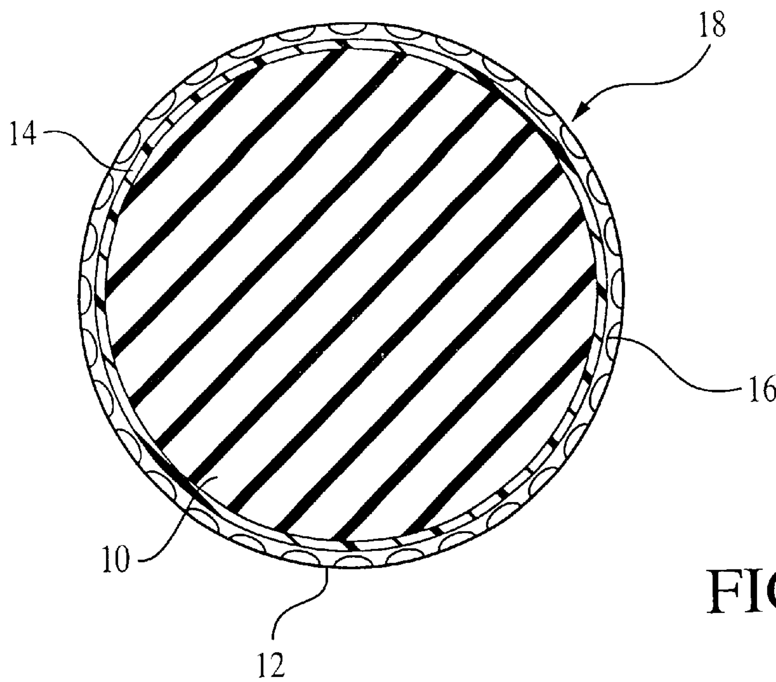


FIG. 1

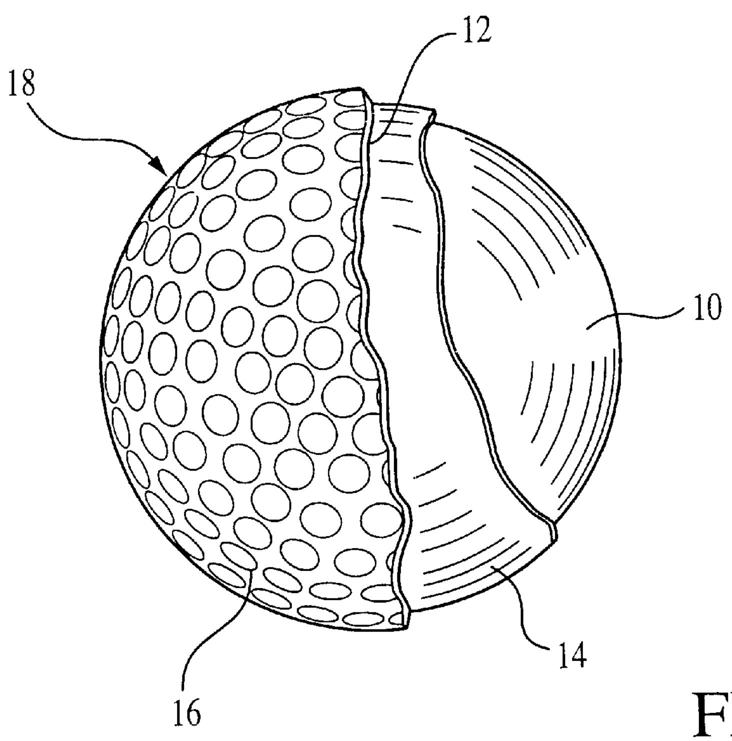


FIG. 2

GOLF BALL HAVING MULTI-LAYER COVER WITH UNIQUE OUTER COVER CHARACTERISTICS

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation application of U.S. application Ser. No. 09/776,278 filed Feb. 2, 2001, which is a continuation application of U.S. application Ser. No. 09/470,196 filed on Dec. 21, 1999, now U.S. Pat. No. 6,210,293, which is a continuation application of U.S. application Ser. No. 08/870,585 filed Jun. 6, 1997 now abandoned, which is a continuation of U.S. application Ser. No. 08/556,237 filed Nov. 9, 1995, now abandoned, which is a continuation-in-part of U.S. application Ser. No. 08/070, 510 filed on Jun. 1, 1993, now abandoned.

FIELD OF THE INVENTION

The present invention relates to golf balls and, more particularly, to improved standard and oversized golf balls comprising multi-layer covers which have a comparatively hard inner layer and a relatively soft outer layer such as that produced by the use of a polyurethane based outer layer. The improved multi-layer golf balls provide for enhanced distance and durability properties over single layer cover golf balls while at the same time offering enhanced "feel" and spin characteristics generally associated with soft balata and balata-like covers of the prior art.

BACKGROUND OF THE INVENTION

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Moreover, the soft balata covers produce a soft "feel" to the low handicap player. Such playability properties (workability, feel, etc.) are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata, balata covered golf balls are easily cut and/or damaged if mis-hit. Golf balls produced with balata or balata-containing cover compositions therefore have a relatively short lifespan.

As a result of this negative property, balata and its synthetic substitutes, transpolyisoprene and transpolybutadiene, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

Ionomeric resins are polymers containing interchain ionic bonding. As result of their toughness, durability and flight characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under the trademark Surlyn® and more recently, by the Exxon Corporation (see U.S. Pat. No. 4,911,451) under the trademarks—"Escor®" and the trade name "lotek®", have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or synthetic) rubbers. As stated, the softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties required for repetitive play.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Metal ions, such as sodium or zinc, are used to neutralize some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, there are currently more than fifty (50) commercial grades of ionomers available both from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc. However, a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved impact resistance and carrying distance properties produced by the "hard" ionomeric resins, but also the playability (i.e., "spin", "feel", etc.) characteristics previously associated with the "soft" balata covers, properties which are still desired by the more skilled golfer.

Consequently, a number of two-piece (a solid resilient center or core with a molded cover) and three-piece (a liquid or solid center, elastomeric winding about the center, and a molded cover) golf balls have been produced by the present inventor and others to address these needs. The different types of materials utilized to formulate the cores, covers, etc. of these balls dramatically alter the balls' overall characteristics.

In addition, multi-layered covers containing one or more ionomer resins have also been formulated in an attempt to produce a golf ball having the overall distance, playability and durability characteristics desired. For example, this was addressed by Spalding & Evenflo Companies, Inc., the assignee of the present invention, in U.S. Pat. No. 4,431,193 where a multi-layered, regular sized, golf ball is disclosed.

In the '193 patent, a multi-layer golf ball is produced by initially molding a first cover layer on a spherical core and then adding a second layer. The first layer is comprised of a hard, high flexural modulus resinous material such as type 1605 Surlyn® (now designated Surlyn® 8940). Type 1605 Surlyn® (Surlyn® 8940) is a sodium ion based low acid (less than or equal to 15 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 51,000 psi. An outer layer of a comparatively soft, low flexural modulus resinous material such as type 1855 Surlyn® (now designated Surlyn® 9020) is molded over the inner cover layer. Type 1855 Surlyn® (Surlyn® 9020) is a zinc ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '193 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a gain in coefficient of restitution over the coefficient of restitution of the core. The increase in the coefficient of restitution provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides essentially no gain in the coefficient of restitution but provides for the advantageous "feel" and playing characteristics of a balata covered golf ball.

Unfortunately, however, while a ball of the '193 patent does exhibit enhanced playability characteristics with improved distance (i.e. enhanced C.O.R. values) over a number of other then known multi-layered balls, the ball suffers from poor cut resistance and relatively short distance (i.e. lower C.O.R. values) when compared to two-piece, single cover layer balls commercially available today. These undesirable properties make the ball produced in accordance with the '193 patent unacceptable by today's standards.

The present invention is directed to new multi-layer golf ball compositions which provide for enhanced coefficient of restitution (i.e, enhanced resilience or carrying distance) and/or durability properties when compared to the multi-layer balls found in the prior art, as well as improved outer cover layer softness and durability. As such, the playability characteristics (i.e., "feel", "click", "spin", etc.) are not diminished.

These and other objects and features of the invention will be apparent from the following summary and description of the invention, the drawings and from the claims.

SUMMARY OF THE INVENTION

The present invention is directed to improved multi-layer golf ball cover compositions and the resulting multi-layer golf balls produced using the improved compositions. The novel multi-layer golf ball covers of the present invention include a first or inner layer or ply of a high acid (greater than 16 weight percent acid) ionomer blend or, more preferably, a low acid (16 weight percent acid or less) ionomer blend and second or outer layer or ply comprised of a comparatively softer, low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane or polyester elastomer. The multi-layer golf balls of the invention can be of standard or enlarged size. Preferably, the inner layer or ply includes a blend of low acid ionomers and has a Shore D hardness of 60 or greater and the outer cover layer comprised of polyurethane and has a Shore D hardness of about 45 (i.e., Shore C hardness of about 65).

It has been found that multi-layer golf balls having inner and outer cover layers exhibit higher C.O.R. values and have greater travel distance in comparison with balls made from a single cover layer. In addition, it has been found that use of an inner cover layer constructed of a blend of low acid (i.e., 16 weight percent acid or less) ionomer resins produces softer compression and higher spin rates than inner cover layers constructed of high acid ionomer resins. This is compounded by the fact that the softer polyurethane outer layer adds to the desirable "feel" and high spin rate while maintaining respectable resiliency. The soft outer layer allows the cover to deform more during impact and increases the area of contact between the club face and the cover, thereby imparting more spin on the ball. As a result, the soft polyurethane cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability.

Consequently, the overall combination of the inner and outer cover layers made from blends of low acid ionomer resins and polyurethane results in a standard size or oversized golf ball having enhanced resilience (improved travel distance) and durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the balls playability properties.

The combination of a low acid ionomer blend inner cover layer with a soft, relatively low modulus ionomer, polyurethane based elastomer outer cover layer provides for good overall coefficient of restitution (i.e., enhanced resilience) while at the same time demonstrating improved compression and spin. The outer cover layer generally contributes to a

more desirable feel and spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Resilience (C.O.R.), along with additional factors such as club head speed, angle of trajectory and ball configuration (i.e., dimple pattern) generally determine the distance a ball will travel when hit. Since club head speed and the angle of trajectory are factors not easily controllable by a manufacturer, factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

The coefficient of restitution (C.O.R.) in solid core balls is a function of the composition of the molded core and of the cover. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings. Although both the core and the cover contribute to the coefficient of restitution, the present invention is directed to the enhanced coefficient of restitution (and thus travel distance) which is affected by the cover composition.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and measuring the ball's incoming and outgoing velocity electronically. As mentioned above, the coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States Golf Association (U.S.G.A.). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Pat. No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests such as the "nine iron" spin rate test described below in the Examples.

Accordingly, the present invention is directed to an improved multi-layer cover which produces, upon molding each layer around a core (preferably a solid core) to formulate a multi-layer cover, a golf ball exhibiting enhanced distance (i.e., resilience) without adversely affecting, and in many instances, improving the ball's playability (hardness/softness) and/or durability (i.e., cut resistance, fatigue resistance, etc.) characteristics.

These and other objects and features of the invention will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional view of a golf ball embodying the invention illustrating a core **10** and a cover **12** consisting of an inner layer **14** and an outer layer **16** having dimples **18**; and

FIG. **2** is a diametrical cross-sectional view of a golf ball of the invention having a core **10** and a cover **12** made of an inner layer **14** and an outer layer **16** having dimple **18**.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to improved multi-layer golf balls, particularly a golf ball comprising a multi-layered cover **12** over a solid core **10**, and method for making same.

The multi-layered cover **12** comprises two layers: a first or inner layer or ply **14** and a second or outer layer or ply **16**. The inner layer **14** is comprised of a low acid (i.e. 16 weight percent acid or less) ionomer blend. Preferably, the inner layer is comprised of a blend of two or more low acid (i.e. 16 weight percent acid or less) ionomer resins neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

The low acid ionomers which may be suitable for use in formulating the inner layer compositions of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10–75%, preferably 30–70%) by the metal ions. Each of the low acid ionomer resins which may be included in the inner layer cover compositions of the invention contains 16% by weight or less of a carboxylic acid.

The inner layer compositions include the low acid ionomers such as those developed and sold by E. I. DuPont de Nemours & Company under the trademark Surlyn® and by Exxon Corporation under the trademarks Escor® or tradename lotek®, or blends thereof.

The low acid ionomeric resins available from Exxon under the designation Escor® and or lotek®, are somewhat similar to the low acid ionomeric resins available under the Surlyn® trademark. However, since the Escor®/lotek® ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc, sodium, magnesium, etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the low acid ionomer blends extend the range of compression and spin rates beyond that previously obtainable. More preferably, it has been found that when two or more low acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further and at an enhanced spin rate than previously known multi-layered golf balls. Such an improvement is particularly noticeable in enlarged or oversized golf balls.

For example, the normal size, multi-layer golf ball taught in U.S. Pat. No. 4,650,193 does not incorporate blends of low acid ionomeric resins of the present invention in the inner cover layer. In addition, the multi-layered ball disclosed in the '193 patent suffers substantially in durability in comparison with the present invention.

Furthermore, as shown in the Examples, use of an inner layer formulated from blends of lower acid ionomers produces multi-layer golf balls having enhanced compression and spin rates. These are the properties desired by the more skilled golfer.

With respect to the outer layer **16** of the multi-layered cover of the present invention, the outer cover layer is comparatively softer than the low acid ionomer blend based inner layer. The softness provides for the enhanced feel and playability characteristics typically associated with balata or balata-blend balls. The outer layer or ply, is comprised of a relatively soft, low modulus (about 1,000 psi to about 10,000 psi) and low acid (less than 16 weight percent acid) ionomer, ionomer blend or a non-ionomeric elastomer such as, but not limited to, a polyurethane, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, a polyurethane sold by BASF under the designation Baytec®or a polyether amide such as that marketed by Elf Atochem S. A. under the trademark Pebax®. The outer layer is fairly thin (i.e. from about 0.010 to about 0.070 in thickness, more desirably 0.03 to 0.06 inches in thickness for a 1.680 inch ball and 0.04 to 0.07 inches in thickness for a 1.72 inch ball), but thick enough to achieve desired playability characteristics while minimizing expense.

Preferably, the outer layer includes a blend of hard and soft (low acid) ionomer resins such as those described in U.S. Pat. Nos. 4,884,814 and 5,120,791, both incorporated herein by reference. Specifically, a desirable material for use in molding the outer layer comprises a blend of a high modulus (hard), low acid, ionomer with a low modulus (soft) low acid, ionomer to form a base ionomer mixture. A high modulus ionomer herein is one which measures from about 15,000 to about 70,000 psi as measured in accordance with ASTM method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240.

A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale.

The hard ionomer resins utilized to produce the outer cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium or lithium salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15–75 percent) neutralized.

The hard ionomeric resins are likely copolymers of ethylene and either acrylic and/or methacrylic acid, with copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

As discussed earlier herein, the hard ionomeric resins introduced under the designation Escor® and sold under the designation lotek® are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However, since the lotek® ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of poly(ethylene-methacrylic acid) some

distinct differences in properties exist. As more specifically indicated in the data set forth below, the hard Iotek® resins (i.e., the acrylic acid based hard ionomer resins) are the more preferred hard resins for use in formulating the outer layer blends for use in the present invention. In addition, various blends of Iotek® and Surlyn® hard ionomeric resins, as well as other available ionomeric resins, may be utilized in the present invention in a similar manner.

Examples of commercially available hard ionomeric resins which may be used in the present invention in formulating the inner and outer cover blends include the hard

sodium ionic copolymer sold under the trademark Surlyn® 8940 and the hard zinc ionic copolymer sold under the trademark Surlyn® 9910. Surlyn® 8940 is a copolymer of ethylene with methacrylic acid and about 15 weight percent acid which is about 29 percent neutralized with sodium ions. This resin has an average melt flow index of about 2.8. Surlyn® 9910 is a copolymer of ethylene and methacrylic acid with about 15 weight percent acid which is about 58 percent neutralized with zinc ions. The average melt flow index of Surlyn® 9910 is about 0.7. The typical properties of Surlyn® 9910 and 8940 are set forth below in Table 1:

TABLE 1

Typical Properties of Commercially Available Hard Surlyn ® Resins Suitable for Use in the Inner and Outer Layer Blends of the Present Invention

	ASTM D	8940	9910	8920	8528	9970	9730
Cation Type		Sodium	Zinc	Sodium	Sodium	Zinc	Zinc
Melt flow index, gm/10 min.	D-1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, g/cm^3	D-792	0.95	0.97	0.95	0.94	0.95	0.95
Hardness, Shore D	D-2240	66	64	66	60	62	63
Tensile Strength, (kpsi), MPa	D-638	(4.8) 33.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(4.1) 28.0
Elongation, %	D-638	470	290	350	450	460	460
Flexural Modulus, (kpsi) MPa	D-790	(51) 350	(48) 330	(55) 380	(32) 220	(28) 190	(30) 210
Tensile Impact (23° C.) KJ/m$_2$(ft.-lbs./in^2)	D-1822S	1020 (485)	1020 (485)	865 (410)	1160 (550)	760 (360)	1240 (590)
Vicat Softening Temperature, ° C.	D-1525	63	62	58	73	61	73

Examples of the more pertinent acrylic acid based hard ionomer resins suitable for use in the present inner and outer cover composition sold under the Iotek® trademark by the Exxon Corporation include Iotek® 4000, Iotek® 4010, Iotek® 8000, Iotek® 8020 and Iotek® 8030. The typical properties of these and other Iotek® hard ionomers suited for use in formulating the inner and outer layer cover composition are set forth below in Table 2:

TABLE 2

Typical Properties of Iotek ® Ionomers

Resin Properties	ASTM Method	Units	4000	4010	8000	8020	8030
Cation type			zinc	zinc	sodium	sodium	sodium
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6	2.8
Density	D-1505	kg/m^3	963	963	954	960	960
Melting Point	D-3417	° C.	90	90	90	87.5	87.5
Crystallization Point	D-3417	° C.	62	64	56	53	55
Vicat Softening Point	D-1525	° C.	62	63	61	64	67
% Weight Acrylic Acid			16		11		
% of Acid Groups cation neutralized			30		40		
Plaque Properties	**ASTM Method**	**Units**	**4000**	**4010**	**8000**	**8020**	**8030**
(3 mm thick, compression molded)							
Tensile at break	D-638	MPa	24	26	36	31.5	28
Yield point	D-638	MPa	none	none	21	21	23
Elongation at break	D-638	%	395	420	350	410	395
1% Secant modulus	D-638	MPa	160	160	300	350	390
Shore Hardness D	D-2240	—	55	55	61	58	59

TABLE 2-continued

Typical Properties of Iotek ® Ionomers

Film Properties (50 micron film 2.2:1 Blow-up ratio)			4000	4010	8000	8020	8030
Tensile at Break							
MD	D-882	MPa	41	39	42	52	47.4
TD	D-882	MPa	37	38	38	38	40.5
Yield point							
MD	D-882	MPa	15	17	17	23	21.6
TD	D-882	MPa	14	15	15	21	20.7
Elongation at Break							
MD	D-882	%	310	270	260	295	305
TD	D-882	%	360	340	280	340	345
1% Secant modulus							
MD	D-882	MPa	210	215	390	380	380
TD	D-882	MPa	200	225	380	350	345
Dart Drop Impact	D-1709	g/micron	12.4	12.5	20.3		

Resin Properties	ASTM Method	Units	7010	7020	7030
Cation type			zinc	zinc	zinc
Melt Index	D-1238	g/10 min.	0.8	1.5	2.5
Density	D-1505	kg/m^3	960	960	960
Melting Point	D-3417	° C.	90	90	90
Crystallization Point	D-3417	° C.	—	—	—
Vicat Softening Point	D-1525	° C.	60	63	62.5
% Weight Acrylic Add					
% of Acid Groups					
Cation Neutralized					

Plaque Properties	ASTM Method	Units	7010	7020	7030
(3 mm thick, compression molded)					
Tensile at break	D-638	MPa	38	38	38
Yield Point	D-638	MPa	none	none	none
Elongation at break	D-638	%	500	420	395
1% Secant modulus	D-638	MPa	—	—	—
Shore Hardness D	D-2240	—	57	55	55

Comparatively, soft ionomers are used in formulating the hard/soft blends of the inner and outer cover compositions. These ionomers include acrylic acid based soft ionomers. They are generally characterized as comprising sodium or zinc salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, acrylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably a zinc based ionomer made from an acrylic acid base polymer in an unsaturated monomer of the acrylate ester class. The soft (low modulus) ionomers have a hardness from about 20 to about 40 as measured on the Shore D scale and a flexural modulus from about 1,000 to about 10,000, as measured in accordance with ASTM method D-790.

Certain ethylene-acrylic acid based soft ionomer resins developed by the Exxon Corporation under the designation lotek® 7520 (referred to experimentally by differences in neutralization and melt indexes as LDX 195, LDX 196, LDX 218 and LDX 219) may be combined with known hard ionomers such as those indicated above to produce the inner and outer cover layers. The combination produces higher C.O.R.s at equal or softer hardness, higher melt flow (which corresponds to improved, more efficient molding, i.e., fewer rejects) as well as significant cost savings versus the inner and outer layers of multi-layer balls produced by other known hard-soft ionomer blends as a result of the lower overall raw materials costs and improved yields.

While the exact chemical composition of the resins to be sold by Exxon under the designation lotek® 7520 is considered by Exxon to be confidential and proprietary information, Exxon's experimental product data sheet lists the following physical properties of the ethylene acrylic acid zinc ionomer developed by Exxon:

TABLE 3

Physical Properties of Iotek ® 7520

Property	ASTM Method	Units	Typical Value
Melt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m^3	0.962
Cation			Zinc
Melting Point	D-3417	° C.	66
Crystallization			

TABLE 3-continued

Physical Properties of Iotek ® 7520

Property	ASTM Method	Units	Typical Value
Point	D-3417	° C.	49
Vicat Softening Point	D-1525	° C.	42
Plaque Properties (2 mm thick Compression Molded Plaques)			
Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	None
Elongation at Break	D-638	%	760
1% Secant Modulus	D-638	MPa	22
Shore D Hardness	D-2240		32
Flexural Modulus	D-790	MPa	26
Zwick Rebound	ISO 4862	%	52
De Mattia Flex Resistance	D-430	Cycles	>5000
Elongation at Break	D412	%	490
Taber Abrasion	D460, H-18	mg/1000 cycles	350

Component[1], Properties	Part A (Isocyanate)	Part B (Resin)
Viscosity @ 25° C., mPa · s	2500	2100
Density @ 25° C., g/cm	1.08	1.09
NCO, %	9.80	—
Hydroxyl Number, Mg KOH/g	—	88

[1]Component A is a modified diphenylmethane diisocyanate (MDI) prepolymer and component B is a polyether polyol blend.

In addition, test data collected by the inventor indicates that lotek® 7520 resins have Shore D hardnesses of about 32 to 36 (per ASTM D-2240), melt flow indexes of 3±0.5 g/10 min (at 190° C. per ASTM D-1288), and a flexural modulus of about 2500–3500 psi (per ASTM D-790). Furthermore, testing by an independent testing laboratory by pyrolysis mass spectrometry indicates that lotek® 7520 resins are generally zinc salts of a terpolymer of ethylene, acrylic acid, and methyl acrylate.

Furthermore, the inventor has found that a newly developed grade of an acrylic acid based soft ionomer available from the Exxon Corporation under the designation lotek® 7510, is also effective, when combined with the hard ionomers indicated above in producing golf ball covers exhibiting higher C.O.R. values at equal or softer hardness than those produced by known hard-soft ionomer blends. In this regard, lotek® 7510 has the advantages (i.e. improved flow, higher C.O.R. values at equal hardness, increased clarity, etc.) produced by the lotek® 7520 resin when compared to the methacrylic acid base soft ionomers known in the art (such as the Surlyn® 8625 and the Surlyn® 8629 combinations disclosed in U.S. Pat. No. 4,884,814).

In addition, lotek® 7510, when compared to lotek® 7520, produces slightly higher C.O.R. valves at equal softness/hardness due to the lotek® 7510's higher hardness and neutralization. Similarly, lotek® 7510 produces better release properties (from the mold cavities) due to its slightly higher stiffness and lower flow rate than lotek® 7520. This is important in production where the soft covered balls tend to have lower yields caused by sticking in the molds and subsequent punched pin marks from the knockouts.

According to Exxon, lotek® 7510 is of similar chemical composition as lotek® 7520 (i.e. a zinc salt of a terpolymer of ethylene, acrylic acid, and methyl acrylate) but is more highly neutralized. Based upon FTIR analysis, lotek® 7520 is estimated to be about 30–40 wt.-% neutralized and lotek® 7510 is estimated to be about 40–60 wt.-% neutralized. The

typical properties of lotek® 7510 in comparison of those of lotek® 7520 are set forth below:

TABLE 4

Physical Properties of Iotek ® 7510 in Comparison to Iotek ® 7520

	IOTEK ® 7520	IOTEK ® 7510
Ml, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Melting Point, ° F.	151	149
Vicat Softening Point, ° F.	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

It has been determined that when hard/soft ionomer blends are used for the outer cover layer, good results are achieved when the relative combination is in a range of about 90 to about 10 percent hard ionomer and about 10 to about 90 percent soft ionomer. The results are improved by adjusting the range to about 75 to 25 percent hard ionomer and 25 to 75 percent soft ionomer. Even better results are noted at relative ranges of about 60 to 90 percent hard ionomer resin and about 40 to 60 percent soft ionomer resin.

Specific formulations which may be used in the cover composition are included in the examples set forth in U.S. Pat. Nos. 5,120,791 and 4,884,814. The present invention is in no way limited to those examples.

Moreover, in alternative embodiments, the outer cover layer formulation may also comprise a soft, low modulus non-ionomeric thermoplastic elastomer including a polyester polyurethane such as B.F.Goodrich Company's Estane® polyester polyurethane X-4517. According to B.F.Goodrich, Estane® X-4517 has the following properties:

Properties of Estane ® X-4517	
Tensile	1430
100%	815
200%	1024
300%	1193
Elongation	641
Youngs Modulus	1826
Hardness A/D	88/39
Dayshore Rebound	59
Solubility in Water	Insoluble
Melt processing temperature	>350° F. (>177° C.)
Specific Gravity (H_2O = 1)	1.1–1.3

Other soft, relatively low modulus non-ionomeric thermoplastic elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced spin characteristics produced by the low acid ionomer resin compositions. Preferably, the non-ionomeric thermoplastic elastomers have a Shore D hardness of 64 or less. These include, but are not limited to thermoplastic polyurethanes such as: Texin® thermoplastic polyurethanes from Mobay Chemical Co. and the Pelletane® thermoplastic polyurethanes from Dow Chemical Co.; Ionomer/rubber blends such as those in Spalding U.S. Pat. Nos. 4,986,545; 5,098,105 and 5,187,013; and, Hytrel® polyester elastomers from DuPont and Pebax® polyesteramides from Elf Atochem S.A.

Similarly, a castable, thermosetting polyurethane produced by BASF under the trade designation Baytec® has also shown enhanced cover formulation properties. According to BASF, Baytec® (such as Baytec® RE 832), relates to a group of reactive elastomers having outstanding wear resistance, high mechanical strength, high elasticity and good resistance to weathering, moisture and chemicals. The Baytec® RE-832 system gives the following typical physical properties:

ASTM Test			
Property	Method	Unit	Value
Tear Strength Die C	D624	psi	180
Stress at			
100% Modulus	D412	psi	320
200% Modulus			460
300% Modulus			600
Ultimate Strength	D412	psi	900
Elongation at Break	D412	%	490
Taber Abrasion	D460, H-18	mg/1000 cycles	350

Component[1] Properties	Part A (Isocyanate)	Part B (Resin)
Viscosity @ 25° C., mPa · s	2500	2100
Density @ 25° C., g/cm	1.08	1.09
NCO, %	9.80	—
Hydroxyl Number, Mg KOH/g	—	88

[1]Component A is a modified diphenylmethane diisocyanate (MDI) prepolymer and component B is a polyether polyol blend.

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core). A comparatively softer outer layer is molded over the inner layer.

The conventional solid core is about 1.545 inches in diameter, although it can range from about 1.495 to about 1.575 inches. Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an α, β, ethylenically unsaturated carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include fillers such as small amounts of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the desired coefficient are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiators such as peroxides are admixed with the core composition so that on the application of heat and pressure, a complex curing cross-linking reaction takes place.

The inner cover layer which is molded over the core is about 0.100 inches to about 0.010 inches in thickness, preferably about 0.0375 inches thick. The outer cover layer is about 0.010 inches to about 0.050 inches in thickness, preferably 0.0300 inches thick. Together, the core, the inner cover layer and the outer cover layer combine to form a ball having a diameter of 1.680 inches or more, the minimum

diameter permitted by the rules of the United States Golf Association and weighing about 1.620 ounces.

Additional materials may be added to the cover compositions (both inner and outer cover layer) of the present invention including dyes (for example, Ultramarine Blue sold by Whitaker, Clark and Daniels of South Plainsfield, N.J.) (see U.S. Pat. No. 4,679,795); pigments such as titanium dioxide, zinc oxide, barium sulfate and zinc sulfate; and UV absorbers; antioxidants; antistatic agents; and stabilizers. Further, the cover compositions of the present invention may also contain softening agents, such as plasticizers, processing aids, etc. and reinforcing material such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers are not impaired.

The various cover composition layers of the present invention may be produced according to conventional melt blending procedures. In the case of the outer cover layer, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the desired additives in a Banbury mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the low acid ionomer resin compositions used to produce the inner cover layer.

The golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the inner cover layer about wound or solid molded cores to produce an intermediate golf ball having a diameter of about 1.50 to 1.67 inches, preferably about 1.620 inches. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.680 inches or more. Although either solid cores or wound cores can be used in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound cores.

In compression molding, the inner cover composition is formed via injection at about 380° F. to about 450° F. into smooth surfaced hemispherical shells which are then positioned around the core in a mold having the desired inner cover thickness and subjected to compression molding at 200° to 30° F. for about 2 to 10 minutes, followed by cooling at 50° to 70° F. for about 2 to 7 minutes to fuse the shells together to form a unitary intermediate ball. In addition, the intermediate balls may be produced by injection molding wherein the inner cover layer is injected directly around the core placed at the center of an intermediate ball mold for a period of time in a mold temperature of from 50° F. to about 100° F. Subsequently, the outer cover layer is molded about the core and the inner layer by similar compression or injection molding techniques to form a dimpled golf ball of a diameter of 1.680 inches or more.

After molding, the golf balls produced may undergo various further processing steps such as buffing, painting and marking as disclosed in U.S. Pat. No. 4,911,451.

The resulting golf ball produced from the low acid ionomer resin inner layer and the relatively softer, low

flexural modulus outer layer provide for an improved multi-layer golf ball which provides for desirable coefficient of restitution, compression, spin and durability properties while at the same time offering the feel characteristics associated with soft balata and balata-like covers of the prior art.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

EXAMPLE 1

Several intermediate balls (cores plus inner cover layers) were prepared in accordance with conventional molding procedures described above. The inner cover compositions were molded around 1.545 inch diameter cores weighing 36.5 grams such that the inner cover had a wall thickness of about 0.0675 inches, with the overall ball measuring about 1.680 inches in diameter.

The cores utilized in the examples were comprised of the following ingredients: high cis-polybutadiene, zinc diacrylate, zinc oxide, zinc stearate, peroxide, calcium carbonate, etc. The molded cores exhibited Riehle compressions of about 60 and C.O.R. values of about 0.800. A representative formulation of the molded cores is set forth below:

MATERIAL	WEIGHT
BR-1220 (high cis-polybutadiene)	70.70
Taktene ® 220 (high cis-polybutadiene)	29.30
React Rite ™ ZDA (zinc diacrylate)	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash (20–40 Mesh)	20.15
Blue Masterbatch	.012
Luperco ® 231XL or Trigonox ® 29/40	.89
Papi ® 94	.50

[1]Blue Masterbatch consists of unknown compositions used only for internal identification purposes and has no effect on physical properties.

The inner cover compositions designated herein as compositions A–E utilized to formulate the intermediate balls are set forth in Table 7 below. The resulting molded intermediate balls were tested to determine the individual compression (Riehle), C.O.R., Shore C hardness, spin rate and cut resistance properties. These results are also set forth in Table 7 below.

The data of these examples are the average of twelve intermediate balls produced for each example. The properties were measured according to the following parameters:

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air cannon at a velocity of 125 feet per second against a steel plate positioned 12 feet from the muzzle of the canon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give a coefficient of restitution.

Shore hardness was measured generally in accordance with ASTM test 2240.

Cut resistance was measured in accordance with the following procedure: A golf ball is fired at 135 feet per second against the leading edge of a pitching wedge wherein

the leading edge radius is 1/32 inch, the loft angle is 51 degrees, the sole radius is 2.5 inches and the bounce angle is 7 degrees.

The cut resistance of the balls tested herein was evaluated on a scale of 1 to 5. The number 1 represents a cut that extends completely through the cover to the core. A 2 represents a cut that does not extend completely through he cover but that does break the surface. A 3 does not break the surface of the cover but does leave a permanent dent. A 4 leaves only a slight crease which is permanent but not as severe as 3. A 5 represents virtually no visible indentation or damage of any sort.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9 iron wherein the club head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110 to 115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

Initial velocity is the velocity of a ball when struck at a hammer speed of 143.8 feet per second in accordance with a test as prescribed by the U.S.G.A.

As will be noted, compositions A, B and C include high acid ionomeric resins (16% or more acid), with composition B further including zinc stearate. Composition D represents the inner layer (i.e. Surlyn® 1605) used in U.S. Pat. No. 4,431,193. Composition E provides a hard, low acid ionomeric resin blend.

The purpose behind producing and testing the balls of Table 5 was to provide a subsequent comparison in properties with the multi-layer golf balls of the present invention.

TABLE 5

Molded Intermediate Golf Balls					
Ingredients of Inner Cover Compositions	A	B	C	D	E
Iotek ® 959	50	50	—	—	—
Iotek ® 960	50	50	—	—	—
Zinc Stearate	—	50	—	—	—
Surlyn ® 8162	—	—	75	—	—
Surlyn ® 8422	—	—	25	—	—
Surlyn ® 1605	—	—	—	100	—
Iotek ® 7030	—	—	—	—	50
Iotek ® 8000	—	—	—	—	50
Properties of Molded Intermediate Balls					
Compression	58	58	60	63	62
C.O.R.	.811	.810	.807	.793	.801
Shore C Hardness	98	98	97	96	96
Spin Rate (R.P.M.)	7,367	6,250	7,903	8,337	7,956
Cut Resistance	4–5	4–5	4–5	4–5	4–5

As shown in Table 5 above, the high acid ionomer resin inner cover layer (molded intermediate balls A–C) have lower spin rates and exhibit higher resiliency characteristics than the low acid ionomer resin based inner cover layers of balls D and E.

Multi-layer balls in accordance with the present invention were then prepared. Specifically, the inner cover compositions used to produce intermediate golf balls from Table 5 were molded over the solid cores to a thickness of about 0.0375 inches, thus forming the inner layer. The diameter of the solid core with the inner layer measured about 1.620 inches. Alternatively, the intermediate golf balls of Table 5 were ground down using a centerless grinding machine to a size of 1.620 inches in diameter to produce an inner cover layer of 0.0375 inches.

The size of 1.620 inches was determined after attempting to mold the outer cover layer to various sizes (1.600", 1.610", 1.620", 1.630"and 1.640") of intermediate (core plus inner layer) balls. It was determined that 1.620"was about the largest "intermediate" ball (i.e., core plus inner layer) which could be easily molded over with the soft outer layer materials of choice. The goal herein was to use as thin an outer layer as necessary to achieve the desired playability characteristics while minimizing the cost of the more expensive outer materials. However, with a larger diameter final golf ball and/or if the cover is compression molded, a thinner cover becomes feasible.

With the above in mind, an outer cover layer composition was blended together in accordance with conventional blending techniques. The outer layer composition used for this portion of the example is a relatively soft cover composition such as those listed in U.S. Pat. No. 5,120,791. An example of such a soft cover composition is a 45% soft/55% hard low acid ionomer blend designated by the inventor as "TE-90". The composition of TE-90 is set forth as follows:

Outer Cover Layer Composition TE-90	
Iotek ® 8000	22.7 weight %
Iotek ® 7030	22.7 weight %
Iotek ® 7520	45.0 weight %
White MB[1]	9.6 weight %

[1]White MB consists of about 23.77 weight percent TiO_2; 0.22 weight percent Uvitex ® OB, 0.03 weight percent Santonox ® R, 0.05 weight percent Ultramarine Blue ™ and 75.85 weight percent Iotek ® 7030.

The above outer layer composition was molded around each of the 1.620 diameter intermediate balls comprising a core plus one of compositions A–D, respectively. In addition, for comparison purposes, Surlyn® 1855 (new Surlyn® 9020), the cover composition of the '193 patent, was molded about the inner layer of composition D (the intermediate ball representative of the '193 patent). The outer layer TE-90 was molded to a thickness of approximately 0.030 inches to produce a golf ball of approximately 1.680 inches in diameter. The resulting balls (a dozen balls for each example) were tested and the various properties thereof are set forth in Table 6A as follows:

TABLE 6A

	Finished Balls				
Ingredients:	1	2	3	4	5
Inner Cover Composition	A	B	C	D	D
Outer Cover Composition	TE-90	TE-90	TE-90	TE-90	Surlyn ® 9020
Properties of Molded Finished Balls:					
Compression	63	63	69	70	61
C.O.R.	.784	.778	.780	.770	.757
Shore C Hardness	88	88	88	88	89
Spin (R.P.M.)	8,825	8,854	8,814	8,990	8,846
Cut Resistance	3–4	3–4	3–4	3–4	1–2

As it will be noted in finished balls 1–4, by creating a multi-layer cover utilizing the high acid ionomer resins in the inner cover layer and the hard/soft low acid ionomer resin in the outer cover layer, higher compression and increased spin rates are noted over the single layer covers of Table 5. In addition, both the C.O.R. and the Shore C hardness are reduced over the respective single layer covers of Table 5. This was once again particularly true with respect to the multi-layered balls containing the high acid ionomer resin in the inner layer (i.e. finished balls 1–4). In addition, with the exception of prior art ball 5 (i.e. the '193 patent), resistance to cutting remains good but is slightly decreased. As noted above, the prior art ball of the '193 patent suffers substantially in durability (as well as in resiliency) in comparison to the balls of the invention.

Furthermore, it is also noted that the use of the high acid ionomer resins as the inner cover material produces a substantial increase in the finished balls' overall distance properties. In this regard, the high acid ionomer resin inner covers of balls 1–3 produce an increase of approximately 10 points in C.O.R. over the low acid ionomer resin inner covers of balls 4 and about a 25 point increase over the prior art balls 5. Since an increase in 3 to 6 points in C.O.R. results in an average increase of about 1 yard in distance, such an improvement is deemed to be significant.

Several other outer layer formulations were prepared and tested by molding them around the core and inner cover layer combination to form balls each having a diameter of about 1.68 inches. First, B.F.Goodrich Estane® X4517 polyester polyurethane was molded about the core molded with inner layer cover formulation A. DuPont Surlyn® 9020 was molded about the core which was already molded with inner layer D. Similar properties tests were conducted on these golf balls and the results are set forth in Table 6B below:

TABLE 6B

	Finish Balls	
Ingredients:	6	7
Inner Cover Layer Composition	A	D
Outer Cover Layer Composition	Estane ® 4517	Surlyn ® 9020

TABLE 6B-continued

	Finish Balls	
Ingredients:	6	7
Properties of Molded Finished Balls:		
Compression	67	61
C.O.R.	.774	.757
Shore C Hardness	74	89
Spin (R.P.M.)	10,061	8,846
Cut Resistance	3–4	1–2

The ball comprising inner layer formulation D and Surlyn® 9020 identifies the ball in the Nesbitt U.S. Pat. No. 4,431,193 patent. As is noted, the example provides for relatively high softness and spin rate though it suffers from poor cut resistance and low C.O.R. This ball is unacceptable by today's standards.

As for the Estane® X4517 polyester polyurethane, a significant increase in spin rate over the TE-90 cover is noted along with an increased compression. However, the C.O.R. and Shore C values are reduced, while the cut resistance remains the same. Furthermore, both the Estane® X4517 polyester polyurethane and the Surlyn® 9020 were relatively difficult to mold in such thin sections.

EXAMPLE 2

In order to analyze the change in characteristics produced by multi-layer golf balls (standard size) having inner cover layers comprised of ionomer resin blends of different acid levels, a series of experiments were run. Specifically, 14 tests were performed, varying the type of core, inner cover layer and outer cover layer. The results are shown below:

PROPERTY	ESCOR ® (IOTEK ®) 959	ESCOR ® (IOTEK ®) 960
Melt Index, g/10 min	2.0	1.8
Cation	Sodium	Zinc
Melting Point, ° F.	172	174
Vicat Softening Point, ° F.	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, the low acid ionomer formulation for SD 90 and Z-Balata are set forth below:

SD Cover	ZB Cover
17.2% Surlyn ® 8320	19% Iotek ® 8000
7.5% Surlyn ® 8120	19% Iotek ® 7030
49% Surlyn ® 9910	52.5% Iotek ® 7520
16.4% Surlyn ® 8940	9.5% white MB
9.7% white MB	

The data clearly indicates that higher C.O.R. and hence increase travel distance can be obtained by using multi-layered covered balls versus balls covered with single layers. However, some sacrifices in compression and spin are also noted. Further, as shown in comparing Example Nos. 12 vs. 13, Example Nos. 17 vs. 16, etc., use of lower acid level inner cover layers and relatively soft outer cover layers (i.e., 50 wt. % or more soft ionomer) produces softer compression and higher spin rates than the golf balls comprised of high acid inner cover layers. Consequently, use of blends of low acid ionomer resins to produce the inner layer of a multi-layer covered golf ball produces not only enhanced travel distance but also enhanced compression and spin properties.

TABLE 7

Sample #	Core	INNER LAYER	THICKNESS	COMP/ COR	OUTER COVER	THICKNESS	COMP (Rhiele)	COR	SHORE D	SPIN
8	1042 YELLOW	NONE	—	SEE BELOW	TOP GRADE	0.055	61	.800	68	7331
9	1042 YELLOW	NONE	—	SEE BELOW	959/960	0.055"	56	.808	73	6516
10	SPECIAL 1.4"	959/960	0/050"	65/.805	959/960	0.055"	48	.830	73	6258
11	1042 YELLOW	NONE	—	SEE BELOW	SD 90	0.055"	62	.792	63	8421
12	SPECIAL 1.4"	TOP GRADE	0.050"	66/.799	SD 90	0.055"	55	.811	63	8265
13	SPECIAL 1.4"	959/960	0.050"	65/.895	SD 90	0.055"	53	.813	63	8254
14	SPECIAL 1.4"	TOP GRADE	0.050"	66/.799	TOP GRADE	0.055"	51	.819	68	7390
15	1042 YELLOW	NONE	—	SEE BELOW	Z-BALATA	0.055"	67	.782	55	9479
16	SPECIAL 1.4"	959/960	0.050"	65/.805	Z-BALATA	0.055"	61	.800	55	9026
17	SPECIAL 1.4"	TOP GRADE	0.050"	66/.799	Z-BALATA	0.055"	60	.798	55	9262

1042 YELLOW > COMP = 72, COR = .780
SPECIAL 147" CORE > COMP = 67, COR = .782

In this regard, Top Grade or TG is a low acid inner cover ionomer resin blend comprising of 70.6% lotek® 8000, 19.9% lotek® 7010 and 9.6% white masterbatch. "959/960" is a 50/50 wt/wt blend of lotek® 959/960. In this regard, Escor® or lotek® 959 is a sodium ion neutralized ethylene-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, lotek® 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

EXAMPLE 3

Multi-layer oversized golf balls were produced utilizing different ionomer resin blends as the inner cover layer (i.e., core plus inner cover layer is defined as "mantel"). The "ball data" of the oversized multi-layer golf balls in comparison with production samples of Top-Flite® XL and Top-Flite® Z-Balata is set forth below.

TABLE 8

	18	19	20	21 Top-Flite ® XL	22 Top-Flite ® Z-Balata 90
Core Data					
Size	1.43	1.43	1.43	1.545	1.545
COR	.787	.787	.787	—	—
Mantle Data					
Material	TG	TG	TG	—	—
Size	1.61	1.61	1.61	—	—
Thickness	.090	.090	.090	—	—
Shore D	68	68	68	—	
Compression	57	57	57	—	—
COR	.815	.815	.815	—	—
Ball Data					
Cover	TG	ZB	SD	TG	ZB
Size	1.725	1.723	1.726	1.681	1.683
Weight	45.2	45.1	45.2	45.3	45.5
Shore D	68	56	63	68	56
Compression	45	55	49	53	77
COR	.820	.800	.810	.809	.797
Spin	7230	9268	8397	7133	9287

The results indicate that use of multi-layer covers enhances C.O.R. and travel distance. Further, the data shows that use of a blend of low acid ionomer resins (i.e., Top Grade) to form the inner cover layer in combination with a soft outer cover (ZB or SD) produces enhanced spin and compression characteristics. The overall combination results in a relatively optimal golf ball with respect to characteristics of travel distances, spin and durability.

EXAMPLE 4

Castable Polyurethane Covered Multi-layer Balls

A limited number of samples were made using BASF Baytec® RE232 polyurethane as a cover material over four different types of mantle cores. Controls included Z-Balata 100s along with the same mantle cores used for the polyurethane samples covered with Z-Balata cover stock. Mantle cores were made up of 82 and 58 compression cores covered with lotek® 8030/7030.

Castable PU Molding Process

Materials used:

Baytec® RE832, mix ratio 9 parts A/12 parts B

1—1.57" i.d. smooth cavity

2—1.68" i.d. dimpled cavities

1—2" hose clamp

1—bench vise or large C-clamp

The mantle core is 1.57" and fits snugly in the 1.57" cavity. The hose clamp is attached to the 1.57' cavity and a mantle core is placed in inside. Urethane is mixed and poured into one of the dimpled cavities and the two halves are placed together and clamped, forcing out excess material and forming half the cover. The hose clamp is used to keep the two mold halves aligned during curing. When the cover material is set up enough (about 5 minutes), the two halves are separated and the 1.57" mold is replaced with the other 1.68" mold and the process is repeated. Both halves of the cover are now cast and the entire assemble is placed in an 125° F. oven for 1 hour after which it can be opened and the ball removed.

All samples were finished using normal production equipment and procedures. The properties of the finished balls are set forth below:

TABLE 9

	23	23	24	25	26	27	28	29
Core Data								
Size	1.47"	1.47"	1.47"	1.47"	1.47	1.47"	1.47"	1.47"
Weight	32.2	32	32.2	32	31.7	32.2	32	32.2
Comp	82	58	82	58	85	82	58	82
COR	768	772	768	772	794	768	772	768
Mantle Data	Iotek ®	Iotek ®	Iotek ®	Iotek ®		Iotek ®	Iotek ®	Iotek ®
Material	8030/7030	8030/7030	8030/7030	8030/7030	None	8030/7030	8030/7030	8030/7030
Weight	37.8	38.1	37.9	38.1		37.8	38.1	37.9
Size	1.57"	1.57"	1.57"	1.57"		1.57"	1.57"	1.57"
Comp	70	48	69	48		70	48	69
COR	781	785	786	788		781	785	786
Ball Data								
Cover Material	Baytec ® RE832	Baytec ® RE832	Baytec ® RE832	Baytec ® RE832	Z-Balata	Z-Balata	Z-Balata	Z-Balata
Weight	45.4	45.5	45.5	45.2	45.3	44.8	45	
Comp	75	64	73	60	80	66	Sn	65
COR	771	763	770	761	792	775	774	778
Shore C	65	65	65	65	84	84	84	84
Spin (rpm)	9560	8789	9285	8780	8796	8702	9072	8643
Cut (1-good, 4-poor)	2	2	2	1.5	2	2	2	2
Scuff (1-good, 4-poor)	1.5	1.5	1.5	1.5	2	3	3	3

Table 9 contains the construction details and test results. Multilayer balls with the thermoset urethane covers (Examples 23–25) were softer in compression and similar in COR to the multi-layer balls with the Z-Balata cover (Examples 27–29). Shore C was much lower for the urethane balls and they were more resistant to scuff than any of the Z-Balata covered balls. Guillotine cut resistance was about the same. Spin rate comparison shows that the urethane samples are better than the Z-Balata covered balls.

Test results indicate that a very good multi-layer ball can be made using castable polyurethane cover material. Further, advantages include the molding of very thin covers, molding over very soft compression core/mantle, and low cost tooling.

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention, be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

I claim:

1. A golf ball comprising:

a core;

an inner cover layer disposed on said core, said inner cover layer having a Shore D hardness of at least 60, said inner cover layer comprising a blend of two or more low acid ionomer resins, each containing no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid; and

an outer cover layer disposed on said inner cover layer, said outer cover layer having a Shore D hardness of about 64 or less, a thickness of from about 0.01 to about 0.07 inches, and comprising a polyurethane material.

2. The golf ball of claim **1** wherein said outer cover layer has a thickness of from about 0.01 to about 0.05 inches.

3. The golf ball of claim **1** wherein said outer cover layer has a thickness of from about 0.03 to about 0.06 inches.

4. A golf ball comprising:

a core:

an inner cover layer disposed about said core, said inner cover layer having a Shore D hardness of at least 60, said inner cover layer comprising a blend of two or more ionomeric resins, each containing no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid; and

an outer cover layer disposed on said inner cover layer, said outer cover layer having a thickness of from about 0.01 to about 0.07 inches, and comprising a polyurethane material.

5. The golf ball of claim **4** wherein said outer cover exhibits a Shore D hardness of about 64 or less.

6. The golf ball of claim **4** wherein said outer cover layer has a thickness of from about 0.01 to about 0.05 inches.

7. The golf ball of claim **4** wherein said outer cover layer has a thickness of from about 0.03 to about 0.06 inches.

8. A golf ball comprising:

a core:

an inner cover layer disposed on said core, said inner cover layer having a Shore D hardness of about 60 or more, said inner cover layer comprising an ionomeric resin including no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi; and

an outer cover layer disposed about said inner cover layer, said outer cover layer having a thickness of from about 0.01 to about 0.07 inches, and comprising a polyurethane material.

9. The golf ball of claim **8** wherein said outer cover exhibits a Shore D hardness of about 64 or less.

10. The golf ball of claim **8** wherein said outer cover layer has a thickness of from about 0.01 to about 0.05 inches.

11. The golf ball of claim **8** wherein said outer cover layer has a thickness of from about 0.03 to about 0.06 inches.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,503,156 B1 Page 1 of 1
DATED : January 7, 2003
INVENTOR(S) : Michael J. Sullivan

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,
Item [63], **Related U.S. Application Data**, "Continuation of application No. 09/776,878, filed on Feb. 2, 2001" should read -- Continuation of application No. 09/776,278, filed on Feb. 2, 2001 --; and
"now Pat. No. 6,210,393" should read -- now Pat. No. 6,210,293 --

Signed and Sealed this

Twenty-eighth Day of October, 2003

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

Exhibit C

US006503130B2

(12) **United States Patent**
Lim

(10) **Patent No.: US 6,503,130 B2**
(45) **Date of Patent: Jan. 7, 2003**

(54) **PROTECTIVE FILM SEPARATOR IN SEMICONDUCTOR WAFER GRINDING PROCESS**

(75) Inventor: **Sang Soon Lim**, Suwon (KR)

(73) Assignee: **Samsung Electronics Co., Ltd.**, Kyungki-do (KR)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/036,404**

(22) Filed: **Jan. 7, 2002**

(65) **Prior Publication Data**

US 2002/0094760 A1 Jul. 18, 2002

(30) **Foreign Application Priority Data**

Jan. 17, 2001 (KR) 01-2681

(51) **Int. Cl.**[7] **B24B 5/00**
(52) **U.S. Cl.** **451/285**; 451/456; 156/344
(58) **Field of Search** 451/41, 285, 287, 451/288, 289, 56, 456; 156/344; 269/762, 21

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,828,640 A * 5/1989 Kaya et al. 156/248
5,268,065 A * 12/1993 Grupen-Shemansky 156/630
6,159,827 A * 12/2000 Kataoka et al. 438/464
6,202,292 B1 * 3/2001 Farnworth et al. 29/743
6,273,791 B1 * 8/2001 Kataoka et al. 451/41
6,436,226 B1 * 8/2002 Omni et al. 156/344

* cited by examiner

Primary Examiner—Eileen P. Morgan
(74) *Attorney, Agent, or Firm*—Lee & Sterba, P.C.

(57) **ABSTRACT**

A protective film separator comprising an adsorption means and a peeling means for removing the protective film in a semiconductor wafer backside grinding process. The adsorption means uses a vacuum to separate a part of a protective film adhered to an electrical circuit patterned side of a wafer from the patterned side of the wafer. The peeling means presses each side of the part of the protective film separated from the wafer by the adsorption means, and separates unpeeled parts thereof from the patterned side of the wafer.

The protective film separator of the present invention reduces costs and expenses for raw materials by eliminating the need for extra removing tape or heat-activated adhesive tape. The present invention may also improve semiconductor yields by reducing the external force applied to a wafer during removal of the protective film, thereby allowing better protection from impurities.

6 Claims, 5 Drawing Sheets

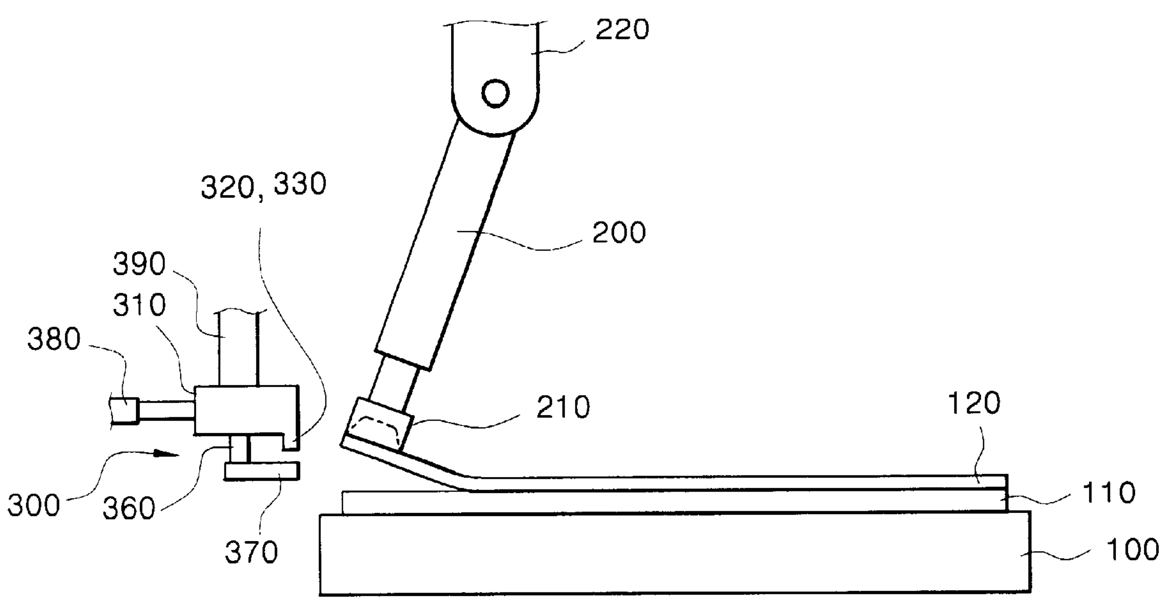
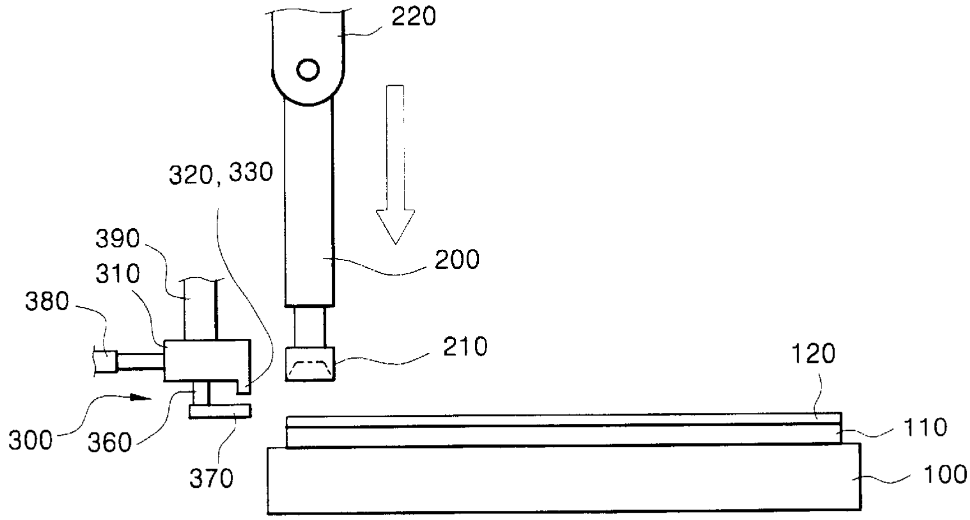


FIG. 1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300
360
370
100

FIG. 2

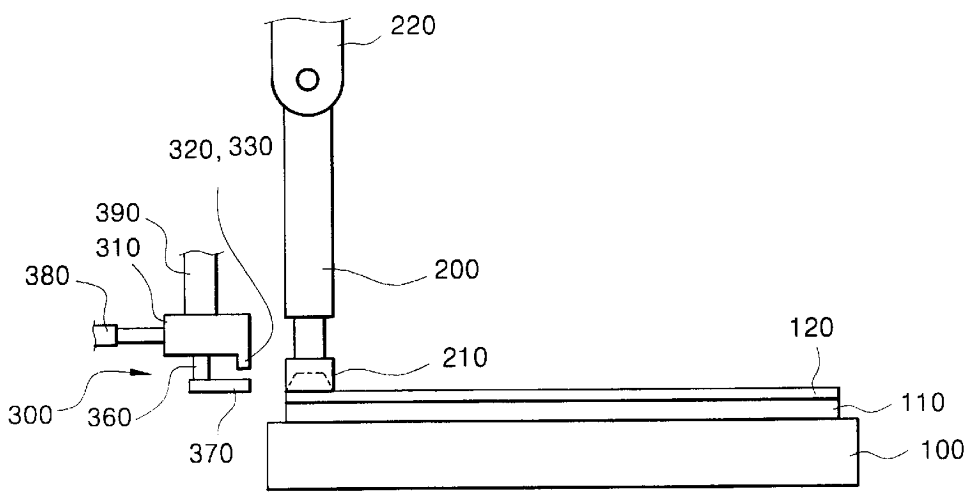
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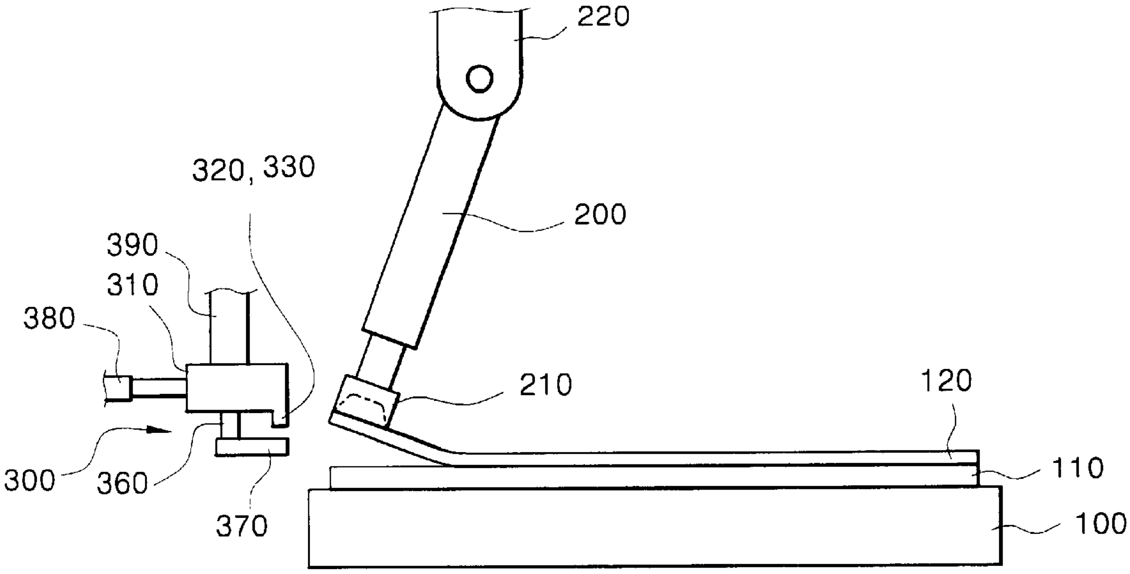
FIG. 3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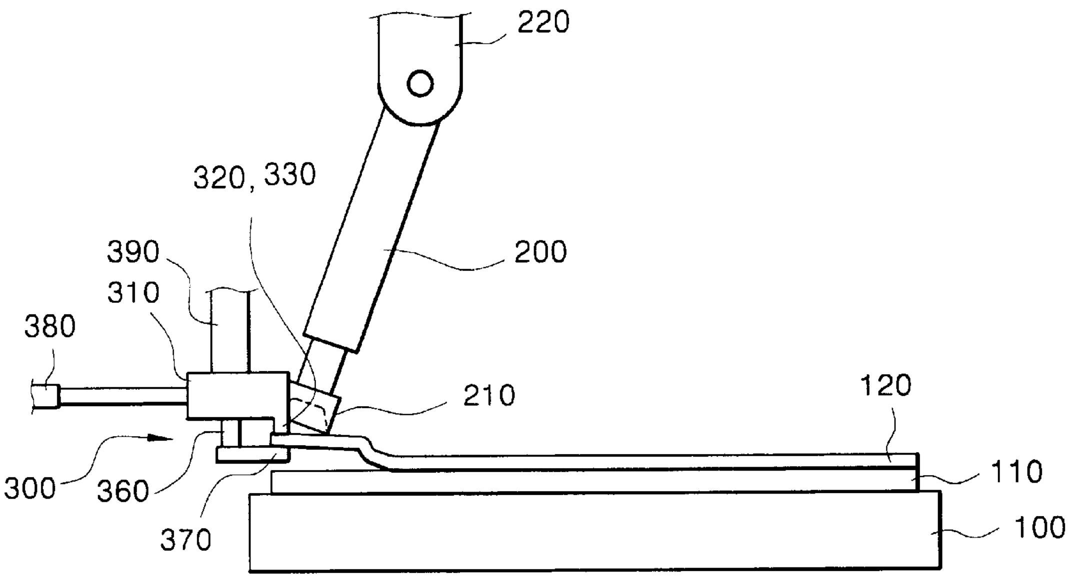
360
100
370

FIG. 4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200
390
310
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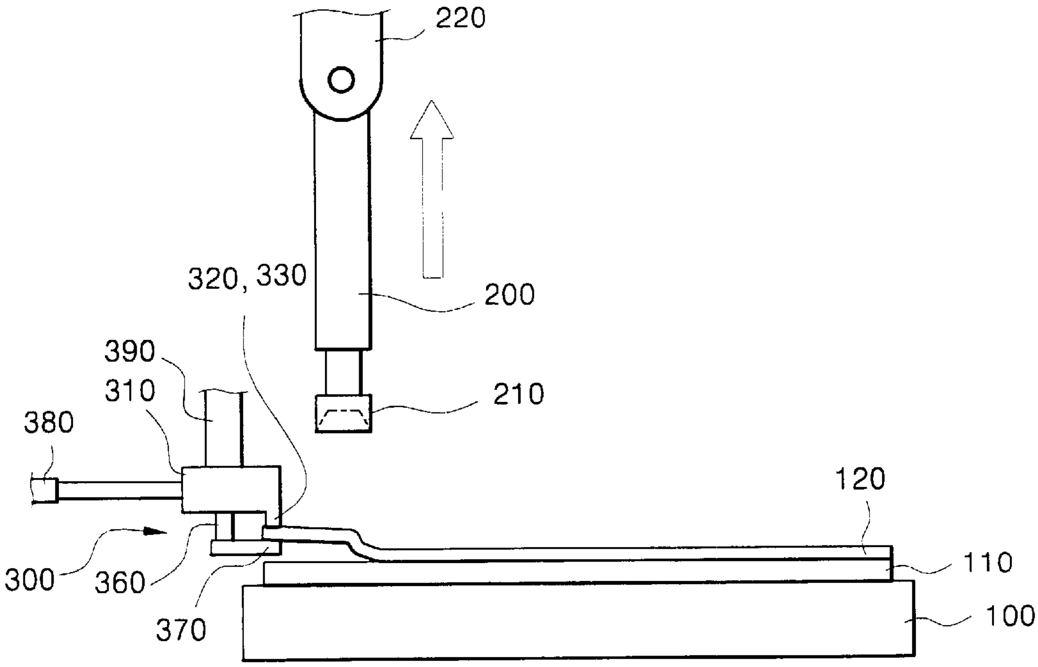
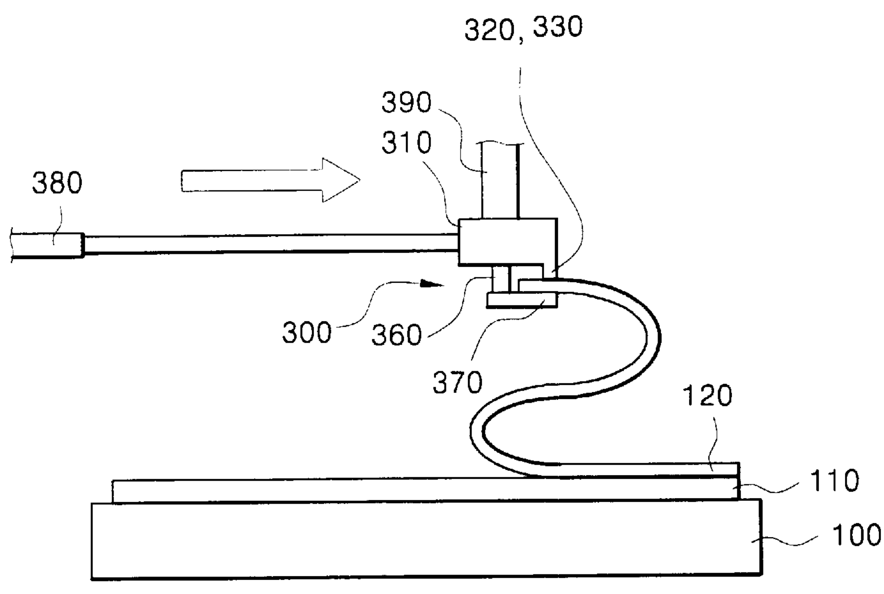
210
120
110
300
360
100
370

FIG. 5



220
320, 330
200
390
310
210
380
120
110
300
360
100
370

FIG. 6



320, 330
390
310
380
300
360
370
120
110
100

FIG.7

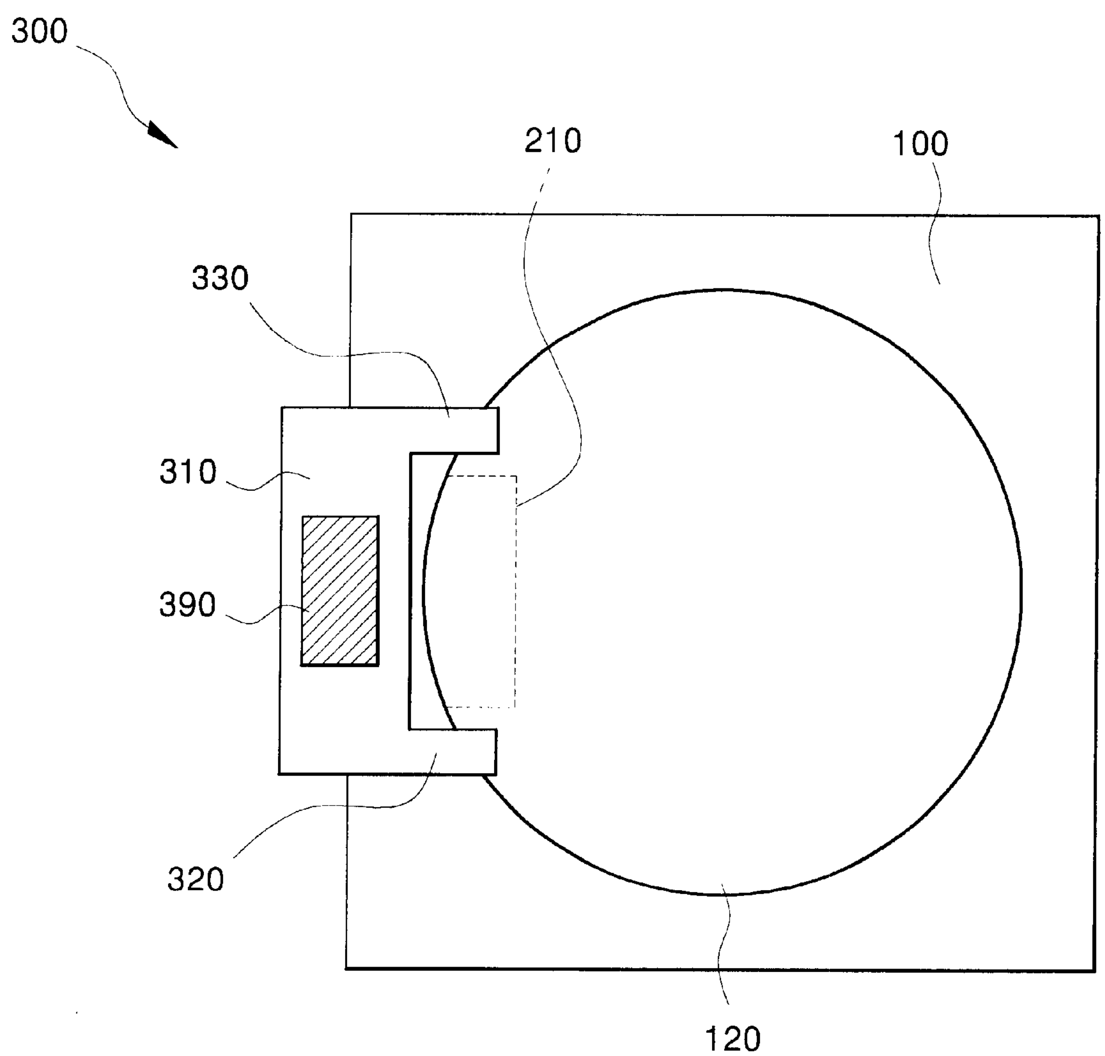
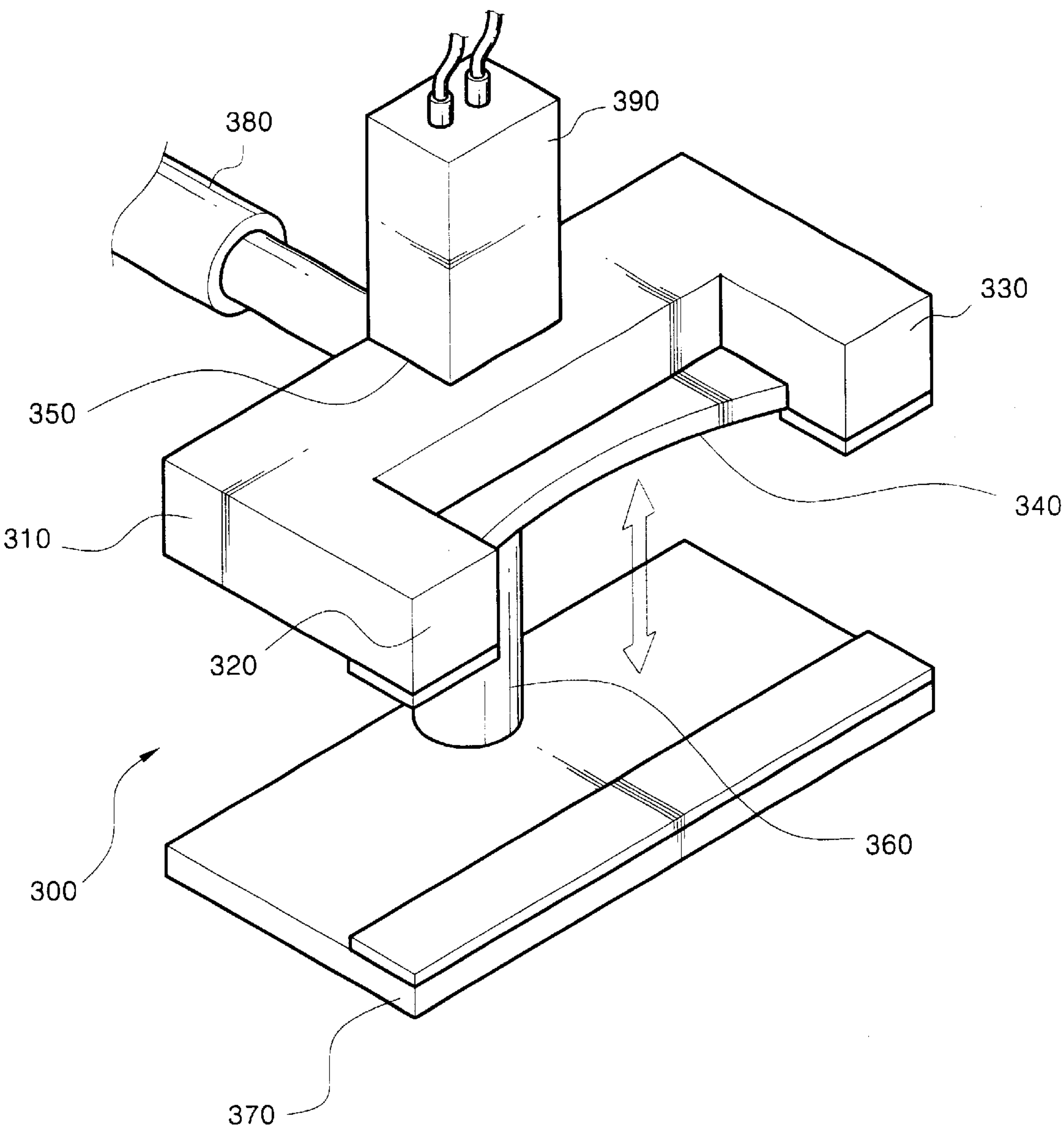


FIG. 8



PROTECTIVE FILM SEPARATOR IN SEMICONDUCTOR WAFER GRINDING PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a protective film separator in a semiconductor wafer grinding process, and more particularly, to a separator for removing a protective film affixed to an electric circuit patterned side of a wafer to protect the wafer in a semiconductor wafer grinding process.

2. Description of Related Art

After completing an electric circuit patterning process to a side of a wafer in a semiconductor process, the other side of the wafer is generally ground in a wafer grinding process.

The wafer grinding process polishes the backside of a wafer and removes a polysilicon layer or an oxide layer that is adhered to the backside of the wafer while the semiconductor process is performed. In addition, the wafer grinding process abrades the backside of a wafer making a thinner wafer, which results in simultaneous improvement in both electric and heat conductivity of a semiconductor device.

Because such a wafer grinding process generates many impurities, a wafer protective film is adhered to the patterned side of a wafer so that the impurities do not cause damage to the electric circuit patterned side of the wafer.

The adhered protective film is removed after completing the wafer grinding process by a protective film separator. Conventionally, two types of protective film separators have generally been used.

The first type of protective film separator attaches an extra removing tape to the adhered protective film and simultaneously irradiates ultraviolet rays to weaken an adhesive strength of the adhered protective film. Then, a roller presses the wafer surface and rotates continuously on the wafer surface to remove the adhered protective film with the extra removing tape.

The second type of protective film separator applies a piece of a heat-activated adhesive tape to a protective film adhered to a wafer surface, and applies heat from a heater to the heat-activated adhesive tape for a few seconds so that the heat-activated adhesive tape adheres to the protective film. Thereafter, the second type of protective film separator irradiates ultraviolet rays to weaken an adhesive strength of the protective film adhered to the wafer, and a tape-removing robot finally removes the protective film with the heat-activated adhesive tape.

The two conventional types of protective film separators continuously consume extra tape, i.e. the extra removing tape and the heat-activated adhesive tape, which causes a continuous increase in the expense of raw materials.

Additionally, either the roller or the heater for removing the protective film presses against the wafer thereby generating severe stress on the wafer surface. Moreover, impurities or residue stained in the protective film can cause damage to the patterned wafer by virtue of the physical contact, which further adversely affects the final wafer yields.

SUMMARY OF THE INVENTION

To overcome the above described problems, a feature of a preferred embodiment of the present invention provides a protective film separator for removing a protective film,

wherein the protective film separator removes the protective film in a semiconductor wafer backside grinding process, thereby eliminating the need for extra removing tape or heat-activated adhesive tape so that the cost of raw materials may be reduced.

Another feature of an embodiment of the present invention provides a protective film separator that reduces an external force applied to a wafer, thereby preventing a patterned side of the wafer from obtaining impurities while the protective film is removed.

In order to achieve the above feaures, preferred embodiments of the present invention provide a protective film separator comprising an adsorption means and a peeling means. The adsorption means applys a vacuum to a part of a protective film adhered to an electric circuit patterened side of a wafer, and separates the part of the protective film from the patterned side of the wafer. The peeling means presses each side of a part of the protective film that has been separated from the wafer by the adsorption means and separates unpeeled parts of the protective film from the patterned side of the wafer.

The peeling means includes a body, top-peeling rods installed in a side of the body, and a bottom-peeling rod. The bottom-peeling rod vertically penetrates the body, moves vertically through the body, and confronts the top-peeling rods in a predetermined interval.

In addition, the top-peeling rods include two top-peeling rods placed apart from each other in a predetermined interval so that the adsorption means is located between a first top-peeling rod and a second top-peeling rod.

The adsorption means includes an adsorption plate in a semi-lunar shape to adhere closely to a rounded edge area of the wafer. The adsorption means also rotates a predetermined angle after adhering to the protective film.

These and other features and aspects of the present invention will be readily apparent to those of ordinary skill in the art upon review of the detailed description that follows." at the end of the Summary of the Invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other features and advantages of the present invention will become more apparent by describing in detail preferred embodiments thereof as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG. **1** illustrates a pre-operational state of a protective film separator for removing a protective film according to a preferred Embodiment of the present invention;

FIG. **2** illustrates a protective film separator according to the present invention in a state where adsorption plate of a vacuum adsorber absorbs a part of the protective film adhered to a wafer;

FIG. **3** illustrates a protective film separator according to the present invention in a state where the vacuum adsorber moves and rotates in a predetermined angle;

FIG. **4** illustrates a protective film separator according to the present invention in a state where the vacuum adsorber absorbs the part of the protective film and a peeling arm simultaneously catches the part of the protective film;

FIG. **5** illustrates a protective film separator according to the present invention in a state where the vacuum adsorber is separated from the part of the protective film, while the peeling arm catches the part of the protective film;

FIG. **6** illustrates a protective film separator according to the present invention in a state where the peeling arm moves to separate remaining parts of the protective film from the wafer;

FIG. **7** illustrates a plan view of a protective film separator according to the present invention in a state where the vacuum adsorber absorbs the part of the protective film and a peeling arm simultaneously catches the part of the protective film; and

FIG. **8** illustrates a perspective view of the peeling arm of the protective film separator for removing a protective film according to the present invention.

DETAILED DESCRIPTION OF PREFFERED EMBODIMENTS

Korean Patent Application No. 2001-2681, filed on Jan. 17, 2001, and entitled: "Protective Film Separator in Semiconductor Wafer Grinding Process", is incorporated by reference herein in its entirety.

The present invention now will be described more fully with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those of ordinary skill in the art.

In general, a semiconductor process includes a single crystal silicon growing process, a device design process, a fabrication FAB process, an assembly process, and an inspection process. The single crystal silicon growing process produces a single crystal silicon ingot with a high purity and slices the single crystal silicon ingot may be sliced into many wafers. After generating photo masks of each layer for a device, the fabrication FAB process employs photo masks to produce electrical circuits on the wafer by generating and etching various layers on the wafer surface. The patterned wafer is sliced into numerous devices during an assembly process so that each of the devices may be combined with a lead frame.

After the wafer fabrication process to pattern an electrical circuit on the wafer surface is performed, a grinding process employing a wafer protective film polishes a thick wafer into a thinner wafer so that electrical conductivity and heat conductivity may be improved simultaneously.

A protective film is adhered to the wafer surface to protect the patterned electrical circuit on the wafer surface from impurities resulting from the grinding process. The protective film is removed when the grinding process is completed.

As illustrated in FIG. **1**, the protective film separator according to the present invention comprises a vacuum adsorber **200** and a peeling arm **300**.

The configuration of the vacuum adsorber **200** will now be explained. A chuck table **100** can move vertically to load a wafer **110**. The vacuum adsorber **200** equipped on an upper side of the chuck table **100** can move vertically and horizontally to remove a protective film **120** adhered to a topside of the wafer **110**. A flexible apparatus **220** installed on a top end of the vacuum adsorber **200** moves and rotates the vacuum adsorber **200** vertically and horizontally.

A semi-lunar shaped adsorption plate **210** equipped at the bottom end of the vacuum adsorber **200** absorbs only a part of an edge area of the wafer **110**. The peeling arm **300** installed nearby the chuck table **100** moves along the upper side of the chuck table **100**, and removes the protective film **120**.

Still referring to FIG. **1**, but also illustrated in FIG. **7** and FIG. **8**, the peeling arm **300** with a body **310** in a hexagonal shape includes a first top-peeling rod **320** and a second top-peeling rod **330**. The first top-peeling rod **320** and the second top-peeling rod **330** protrude from both sides of the body **310** toward the upward facing side of the wafer **110**. A width between the first top-peeling rod **320** and the second top-peeling rod **330** is sufficient to accommodate the adsorption plate **210** of the vacuum adsorber **200**. A concave surface **340** (see FIG. **8**) in a side of the body **310** formed between the first top-peeling rod and the second top-peeling rod corresponds to the semi-lunar shaped adsorption plate **210** of the vacuum adsorber **200** so that the adsorption plate **210** may be accomodated between the two top-peeling rods.

A penetration hole **350** (see FIG. **8**) in a center of the body **310** equips a driving cylinder **390**. The driving cylinder **390** can move a driving rod **360** installed in a bottom side of the driving cylinder **390** in a vertical direction.

A bottom-peeling rod **370** with a considerable width is located at a bottom end of the driving rod **360** and protrudes in a same direction as the first top-peeling rod **320** and the second top-peeling rod **330**.

Therefore, a distance between the bottom-peeling rod **370** and the two top-peeling rods **320** and **330** can be changed reversibly to catch the protective film **120**, while the body **310** halts and the driving rod **360** moves vertically. A transfer cylinder **380** allows the body **310** to move horizontally along the upper side of the wafer **110**.

According to a preferred embodiment of the present invention, a transfer apparatus that moves the body **310** horizontally may employ a transfer robot with a multi-axis arm structure besides the transfer cylinder **380**, and may also employ different types of apparatuses.

Referring to FIG. **1**–FIG. **6**, an operation of the protective film separator for removing a wafer protective film according to a preferred embodiment of the present invention will now be described.

FIG. **1** illustrates a view of a pre-operational state of the protective film separator for removing the protective film according to a preferred embodiment of the present invention. The wafer **110** illustrated in FIG. **1** is loaded on the table **100** after a wafer grinding process is performed. At this time, the vacuum adsorber **200** is placed at an upper side of an edge area of the wafer **110**, and the peeling arm **300** is located outside of the wafer **110**.

FIG. **2** illustrates the next operation. The vacuum adsorber **200** moves down so that the adsorption plate **210** of the vacuum adsorber **200** may adhere closely to the edge area of the wafer **110**. Then, the vacuum adsorber **200** applies a vacuum as an adsorption force to the protective film **120**, thereby allowing the adsorption plate **210** to apply an upward external adsorption force to the protective film **120**.

When the adsorption force is supplied to the protective film **120** through the vacuum adsorber **200**, the vacuum adsorber **200** adsorbs the protective film **120** as illustrated in FIG. **3**, and rotates a predetermined angle to the inside of the wafer **110** by the flexible apparatus **220** installed at a top end of the vacuum adsorber **200**.

Preferably, the predetermined angle of rotation in the vacuum adsorber **200** is around 20°. Then, the adsorption plate **210** peels a part of the protective film **120** off the surface of the wafer **110**.

When a part of the protective film **120** is peeled off, as illustrated in FIG. **4**, the body **310** moved by the driving cylinder **390** places the peeling rods **320**, **330** and **370** of the

peeling arm **300** on surfaces of the peeled part of the protective film **120**.

Then, the adsorption plate **210** of the vacuum adsorber **200** is placed in the concave surface **340** (see FIG. **8**) of the body **310** between the two peeling rods **320** and **330**. When the driving cylinder **390** moves the driving rod **360** in an upward direction, the bottom-peeling rod **370** also moves in an upward direction, so that the peeled part of the protective film **120** is pressed between the upper and lower peeling rods **320**, **330** and **370**.

As illustrated in FIG. **5**, the vacuum adsorber **200** no longer applies the adsorption force to the protective film **120**, and is separated from the protective film **120**.

Finally, as illustrated in FIG. **6**, the vacuum adsorber **200** is moved to an initial position, and the peeling rods **320**, **330** and **370** in the peeling arm **300** press the peeled part of the protective film **120**, and move in a direction of the unpeeled protective film **120** by the transfer cylinder **380**. Therefore, the peeling rods **320**, **330** and **370** peel the adhered protective film **120** off the surface of the wafer **110** and remove the protective film **120** from the wafer **110**.

As described in the above statements, the protective film separator for removing a wafer protective film comprises the vacuum adsorber **200** and the peeling arm **300** pressing a peeled part of the protective film **120** to remove an unpeeled part of the protective film **120**.

Therefore, the protective film separator for removing a wafer protective film according to a preferred embodiment of the present invention does not employ extra removing tape or heat-activated adhesive tape to remove a protective film after the wafer grinding process. As a result, expenses for raw materials in a semiconductor fabrication process are reduced. In addition, the external force on the wafer is reduced and a patterned surface of a wafer can be better protected from impurities, and thereby improve semiconductor wafer fabrication yields.

A preferred embodiment of the present invention has been disclosed herein and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purpose of limitation. Accordingly, it will be understood

by those of ordinary skill in the art that various changes in form and details may be made without departing from the spirit and scope of the invention as set forth in the following claims.

What is claimed is:

1. A protective film separator in a semiconductor wafer grinding process, the protective film separator comprising:

an adsorption means applying a vacuum to a part of a protective film adhered in an electrical circuit patterned side of a wafer, and separating the part of the protective film from the patterned side of the wafer; and

a peeling means pressing each side of the part of the protective film separated from the wafer by the adsorption means, and separating unpeeled parts of the protective film from the patterned side of the wafer.

2. The protective film separator of claim **1**, wherein the peeling means comprises:

a body;

more than one top-peeling rod installed on a side of the body; and

a bottom-peeling rod penetrating the body vertically, moving vertically through the body, and confronting the top-peeling rod in a predetermined interval.

3. The protective film separator of claim **2**, wherein the top-peeling rods include a first top-peeling rod and a second top-peeling rod placed a predetermined distance apart from each other so that the adsorption means may be located between the first top-peeling rod and the second top-peeling rod.

4. The protective film separator of claim **1**, wherein the adsorption means includes a semi-lunar shaped adsorption plate to adhere closely to a rounded edge area of the wafer.

5. The protective film separator of claim **2**, wherein the adsorption means includes a semi-lunar shaped adsorption plate to adhere closely to a rounded edge area of the wafer.

6. The protective film separator of claim **1**, wherein the adsorption means rotates a predetermined angle after adhering to the protective film.

* * * * *

Exhibit D

US006595873B2

(12) **United States Patent**
Sullivan

(10) **Patent No.: US 6,595,873 B2**
(45) **Date of Patent: *Jul. 22, 2003**

(54) **MULTI-LAYER GOLF BALL**

(75) Inventor: **Michael J. Sullivan**, Chicopee, MA (US)

(73) Assignee: **Spalding Sports Worldwide, Inc.**, Chicopee, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/776,278**

(22) Filed: **Feb. 2, 2001**

(65) **Prior Publication Data**

US 2003/0017889 A1 Jan. 23, 2003

Related U.S. Application Data

(63) Continuation of application No. 09/470,196, filed on Dec. 21, 1999, now Pat. No. 6,210,293, which is a continuation of application No. 08/870,585, filed on Jun. 6, 1997, now abandoned, which is a continuation of application No. 08/556,237, filed on Nov. 9, 1995, now abandoned, which is a continuation-in-part of application No. 08/070,510, filed on Jun. 1, 1993, now abandoned.

(51) **Int. Cl.**[7] **A63B 37/12**
(52) **U.S. Cl.** **473/374**
(58) **Field of Search** 473/373, 374, 473/370, 371, 372, 376, 377, 378

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,741,480 A	4/1956	Smith
2,973,800 A	3/1961	Muccino
3,053,539 A	9/1962	Piechowski
3,264,272 A	8/1966	Rees
3,313,545 A	4/1967	Bartsch
3,373,123 A	3/1968	Brice
3,384,612 A	5/1968	Brandt et al.
3,395,109 A	7/1968	Molitor et al.
3,458,205 A	7/1969	Smith et al.
3,502,338 A	3/1970	Cox
3,534,965 A	10/1970	Harrison et al.

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

CA	2137841	6/1995
EP	0589647	3/1994
EP	0630665	12/1994
EP	0637459	2/1995
GB	494031	10/1938
GB	2245580	1/1992
GB	2248067	3/1992
GB	2264302	11/1992
GB	2291811	2/1996
GB	2291812	2/1996

OTHER PUBLICATIONS

A General Reference Manual, "The Chemistry of Polyurethane Coatings", Mobay Corporation, 1–16 (1988).

Product Announcement, "New Polyurea System Offering Rapid Mold Times and Excellent Thermal Stability for Automotive Fascias Is Introduced by Mobay," PRNewswire, Mar. 1, 1998.

Cytec Industries, Inc., "TMXDI®(META) Aliphatic Isocyanates," brochure, pp. 2–11, 9/94.

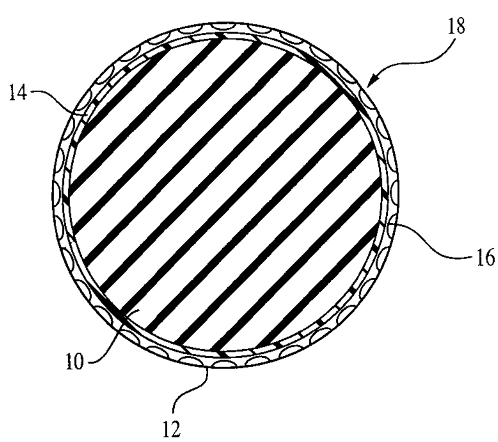
(List continued on next page.)

Primary Examiner—Mark S. Graham
Assistant Examiner—Raeann Gorden

(57) **ABSTRACT**

The present invention is directed to an improved multi-layer golf ball comprising a core, an inner cover layer and an outer cover layer. The inner cover layer is comprised of a low acid ionomer blend which may or may not include a filler such as zinc-stearate. The outer cover layer is comprised of a soft, non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane, polyester or polyesteramide. The resulting multi-layered golf ball of the present invention provides for enhanced distance without sacrificing playability or durability when compared to known multi-layer golf balls.

6 Claims, 1 Drawing Sheet



U.S. PATENT DOCUMENTS

3,572,721 A 3/1971 Harrison et al.
3,883,145 A 5/1975 Cox et al.
3,979,126 A 9/1976 Dusbiber
3,989,568 A 11/1976 Isaac
4,076,255 A 2/1978 Moore et al.
4,085,937 A 4/1978 Schenk
4,123,061 A 10/1978 Dusbiber
4,190,711 A 2/1980 Zdrahala et al.
4,218,543 A 8/1980 Weber et al.
4,248,432 A 2/1981 Hewitt et al.
4,272,079 A 6/1981 Nakade et al.
4,274,637 A 6/1981 Molitor
4,337,946 A 7/1982 Saito et al.
4,431,193 A * 2/1984 Nesbitt 473/373
4,442,282 A 4/1984 Kolycheck
4,570,937 A 2/1986 Yamada
4,582,887 A 4/1986 Dominguez et al.
4,590,219 A 5/1986 Nissen et al.
4,607,090 A 8/1986 Dominguez
4,650,193 A 3/1987 Molitor et al.
4,674,751 A 6/1987 Molitor et al.
4,679,795 A 7/1987 Melvin et al.
4,688,801 A 8/1987 Reiter
4,690,981 A 9/1987 Statz
4,695,055 A 9/1987 Newcomb et al.
4,714,253 A 12/1987 Nakahara et al.
4,762,322 A 8/1988 Molitor et al.
4,798,386 A 1/1989 Berard
4,848,770 A 7/1989 Shama
4,852,884 A 8/1989 Sullivan
4,858,923 A 8/1989 Gobush et al.
4,858,924 A 8/1989 Saito et al.
4,878,674 A 11/1989 Newcomb et al.
4,884,814 A * 12/1989 Sullivan 473/378
4,911,451 A 3/1990 Sullivan et al.
4,919,434 A 4/1990 Saito
4,957,297 A 9/1990 Newcomb et al.
4,979,746 A 12/1990 Gentiluomo
4,984,804 A 1/1991 Yamada et al.
4,986,545 A 1/1991 Sullivan
5,002,281 A 3/1991 Nakahara et al.
5,006,297 A 4/1991 Brown et al.
5,019,319 A 5/1991 Nakamura et al.
5,026,067 A 6/1991 Gentiluomo
5,035,425 A 7/1991 Edwards
5,045,591 A 9/1991 Meyer et al.
5,048,838 A 9/1991 Chikaraishi et al.
5,068,151 A * 11/1991 Nakamura 473/374
5,072,944 A 12/1991 Nakahara et al.
5,096,201 A 3/1992 Egashira et al.
5,098,105 A 3/1992 Sullivan
5,104,126 A 4/1992 Gentiluomo
5,120,791 A 6/1992 Sullivan
5,142,835 A 9/1992 Mrocca
5,150,906 A 9/1992 Molitor et al.
5,156,405 A 10/1992 Kitaoh et al.
5,184,828 A 2/1993 Kim et al.
5,187,013 A 2/1993 Sullivan
5,197,740 A 3/1993 Pocklington et al.
5,219,973 A 6/1993 Slack et al.
5,222,739 A 6/1993 Horiuchi et al.
5,244,969 A 9/1993 Yamada
5,253,871 A 10/1993 Viollaz
5,273,286 A 12/1993 Sun
5,273,287 A 12/1993 Molitor et al.
5,274,041 A 12/1993 Yamada
5,281,651 A 1/1994 Arjunan et al.
5,300,334 A 4/1994 Niederst et al.
5,304,608 A 4/1994 Yabuki et al.
5,306,760 A 4/1994 Sullivan
5,312,857 A 5/1994 Sullivan
5,314,187 A * 5/1994 Proudfit 473/373
5,324,783 A 6/1994 Sullivan
5,330,837 A 7/1994 Sullivan
5,334,673 A * 8/1994 Wu 473/378
5,338,610 A 8/1994 Sullivan
5,368,304 A 11/1994 Sullivan et al.
5,368,806 A 11/1994 Harasin et al.
5,387,470 A * 2/1995 Parnell 428/215
5,387,750 A 2/1995 Chiang
5,403,010 A 4/1995 Yabuki et al.
5,439,227 A 8/1995 Egashira et al.
5,480,155 A 1/1996 Molitor et al.
5,482,285 A 1/1996 Yabuki et al.
5,484,870 A 1/1996 Wu
5,490,673 A 2/1996 Hiraoka
5,490,674 A 2/1996 Hamada et al.
5,492,972 A 2/1996 Stefani
5,553,852 A 9/1996 Higuchi et al.
5,586,950 A 12/1996 Endo
5,628,699 A 5/1997 Maruko et al.
5,668,239 A 9/1997 Nodelman et al.
5,674,137 A 10/1997 Maruko et al.
5,688,191 A 11/1997 Cavallaro et al.
5,692,974 A 12/1997 Wu et al.
5,730,665 A 3/1998 Shimosaka et al.
5,733,206 A 3/1998 Nesbitt et al.
5,733,207 A 3/1998 Sullivan et al.
5,733,428 A 3/1998 Calabria et al.
5,739,247 A 4/1998 Lesko et al.
5,739,253 A 4/1998 Nodelman et al.
5,750,580 A 5/1998 Mayer et al.
5,759,676 A 6/1998 Cavallaro et al.
5,779,561 A 7/1998 Sullivan et al.
5,779,562 A 7/1998 Melvin et al.
5,779,563 A 7/1998 Yamagishi et al.
5,783,293 A 7/1998 Lammi
5,792,008 A 8/1998 Kakiuchi et al.
5,797,808 A 8/1998 Hayashi et al.
5,800,284 A 9/1998 Sullivan et al.
5,803,831 A 9/1998 Sullivan et al.
5,810,678 A 9/1998 Cavallaro et al.
5,813,923 A 9/1998 Cavallaro et al.
5,816,937 A 10/1998 Shimosaka et al.
5,820,488 A 10/1998 Sullivan et al.
5,820,489 A 10/1998 Sullivan et al.
5,820,491 A 10/1998 Hatch et al.
5,827,167 A 10/1998 Dougan et al.
5,830,087 A 11/1998 Sullivan et al.
5,833,553 A 11/1998 Sullivan et al.
5,833,554 A 11/1998 Sullivan et al.
5,836,833 A 11/1998 Shimosaka et al.
5,849,168 A 12/1998 Lutz
5,856,388 A 1/1999 Harris et al.
5,863,264 A 1/1999 Yamagishi et al.
5,873,796 A 2/1999 Cavallaro et al.
5,885,172 A 3/1999 Hebert et al.
5,888,437 A 3/1999 Calabria et al.
5,891,973 A 4/1999 Sullivan et al.
5,897,884 A 4/1999 Calabria et al.
5,899,822 A 5/1999 Yamagishi et al.
5,902,192 A 5/1999 Kashiwagi et al.
5,908,358 A 6/1999 Wu
5,919,100 A 7/1999 Boehm et al.
5,919,862 A 7/1999 Rajagopalan
5,922,252 A 7/1999 Stanton et al.
5,929,189 A 7/1999 Ichikawa et al.
5,935,021 A 8/1999 Kashiwagi et al.
5,947,842 A 9/1999 Cavallaro et al.
5,947,843 A 9/1999 Calabria et al.
5,959,059 A 9/1999 Vedula et al.

5,976,035	A	11/1999	Umezawa et al.	
5,984,807	A	11/1999	Wai et al.	
6,210,293	B1 *	4/2001	Sullivan	473/374

OTHER PUBLICATIONS

Bayer Corporation, "Engineering Polymers RIM and Part Mold Design," brochure, pp. 1–85, 5/95.

Bayer Corporation, "Engineering Polymers Properties Guide Thermoplastics and Polyurethanes," brochure, pp. 2–7, 28–29.

A Properties Group, "Engineering Polymers Thermoplastics and Thermosets," Miles Inc., 1–23 (1994).

Polyurethane Handbook, "Chemistry–Raw Materials–Processing Applications–Proeprties," edited by Oertel et al., Hanser/Gardner Publications, Inc., 101, 102 (1994).

Tanslated Claims for JP 1,795,357 publ. Jan. 19, 1993.

DuPont NUCREL 035 Resin, DuPont Company, Wilmington, DE 1989 (no date).

ESCOR Acid Terpolymers, EXXON Chemical Co.

Translated claims for JP 1,771,941 publ. Aug. 6, 1992.

* cited by examiner

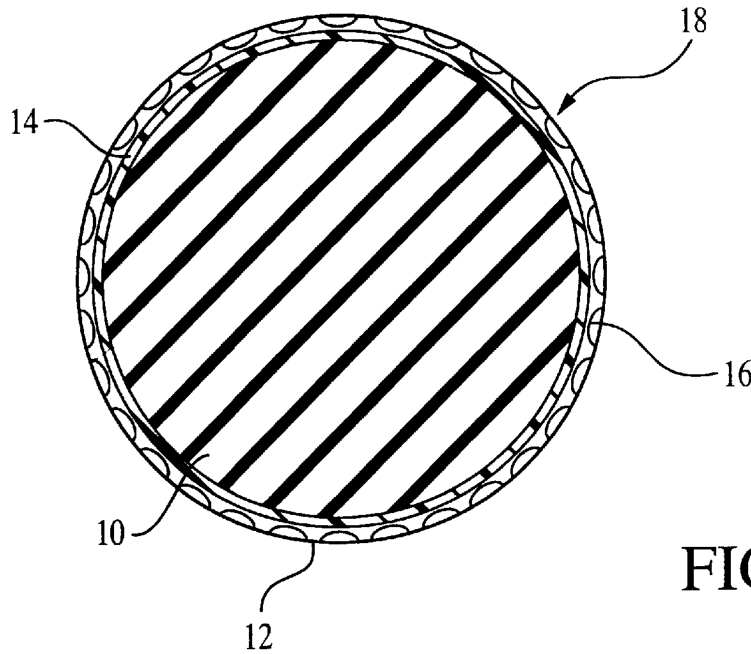


FIG. 1

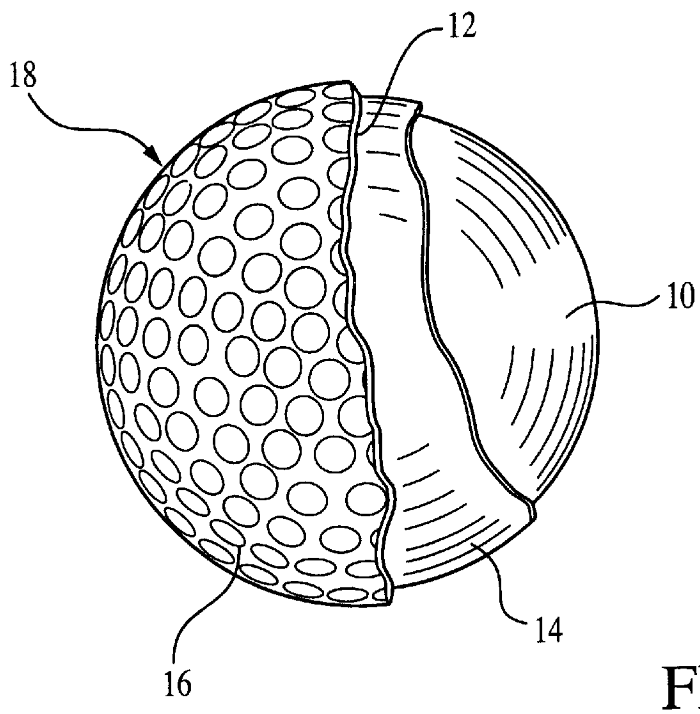


FIG. 2

MULTI-LAYER GOLF BALL

FIELD OF THE INVENTION

This application is a continuation application of U.S. application Ser. No. 09/470,196 filed Dec. 21, 1999, now U.S. Pat. No. 6,210,293, which is a continuation application of U.S. application Ser. No 08/870,585 filed Jun. 6, 1997, now abandoned, which is a continuation application of U.S. application Ser. No. 08/556,237 filed on Nov. 9, 1995, now abandoned, which is a continuation-in-part of U.S. application Ser. No. 08/070,510 filed Jun. 1, 1993, now abandoned.

The present invention relates to golf balls and, more particularly, to improved standard and oversized golf balls comprising multi-layer covers which have a comparatively hard inner layer and a relatively soft outer layer such as that produced by the use of a polyurethane based outer layer. The improved multi-layer golf balls provide for enhanced distance and durability properties over single layer cover golf balls while at the same time offering enhanced "feel" and spin characteristics generally associated with soft balata and balata-like covers of the prior art.

BACKGROUND OF THE INVENTION

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Moreover, the soft balata covers produce a soft "feel" to the low handicap player. Such playability properties (workability, feel, etc.) are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata, balata covered golf balls are easily cut and/or damaged if mis-hit. Golf balls produced with balata or balata-containing cover compositions therefore have a relatively short lifespan.

As a result of this negative property, balata and its synthetic substitutes, transpolyisoprene and trans-polybutadiene, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

Ionomeric resins are polymers containing interchain ionic bonding. As a result of their toughness, durability and flight characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and more recently, by the Exxon Corporation (see U.S. Pat. No. 4,911,451) under the trademarks—"Escor®" and the trade name "Iotek", have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or synthetic) rubbers. As stated, the softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties required for repetitive play.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Metal ions, such as sodium or zinc, are used to neutralize some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced

properties, i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, while there are currently more than fifty (50) commercial grades of ionomers available both—from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc, a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved impact resistance and carrying distance properties produced by the "hard" ionomeric resins, but also the playability (i.e., "spin", "feel", etc.) characteristics previously associated with the "soft" balata covers, properties which are still desired by the more skilled golfer.

Consequently, a number of two-piece (a solid resilient center or core with a molded cover) and three-piece (a liquid or solid center, elastomeric winding about the center, and a molded cover) golf balls have been produced by the present inventor and others to address these needs. The different types of materials utilized to formulate the cores, covers, etc. of these balls dramatically alters the balls' overall characteristics.

In addition, multi-layered covers containing one or more ionomer resins have also been formulated in an attempt to produce a golf ball having the overall distance, playability and durability characteristics desired. For example, this was addressed by Spalding & Evenflo Companies, Inc., the assignee of the present invention, in U.S. Pat. No. 4,431,193 where a multi-layered regular sized, golf ball is disclosed.

In the '193 patent, a multi-layer golf ball is produced by initially molding a first cover layer on a spherical core and then adding a second layer. The first layer is comprised of a hard, high flexural modulus resinous material such as type 1605 Surlyn® (now designated Surlyn® 8940). Type 1605 Surlyn® (Surlyn® 8940) is a sodium ion based low acid (less than or equal to 15 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 51,000 psi. An outer layer of a comparatively soft, low flexural modulus resinous material such as type 1855 Surlyn® (now designated Surlyn® 9020) is molded over the inner cover layer. Type 1855 Surlyn® (Surlyn® 9020) is a zinc ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '193 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a gain in coefficient of restitution over the coefficient of restitution of the core. The increase in the coefficient of restitution provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides essentially no gain in the coefficient of restitution but provides for the advantageous "feel" and playing characteristics of a balata covered golf ball.

Unfortunately, however, while a ball of the '193 patent does exhibit enhanced playability characteristics with improved distance (i.e. enhanced C.O.R. values) over a number of other then known multi-layered balls, the ball suffers from poor cut resistance and relatively short distance (i.e. lower C.O.R. values) when compared to two-piece, single cover layer balls commercially available today. These undesirable properties make the ball produced in accordance with the '193 patent unacceptable by today's standards.

The present invention is directed to new multi-layer golf ball compositions which provide for enhanced coefficient of restitution (i.e, enhanced resilience or carrying distance) and/or durability properties when compared to the multi-layer balls found in the prior art, as well as improved outer cover layer softness and durability. As such, the playability characteristics (i.e., "feel", "click", "spin", etc.) are not diminished.

These and other objects and features of the invention will be apparent from the following summary and description of the invention, the drawings and from the claims.

SUMMARY OF THE INVENTION

The present invention is directed to improved multi-layer golf ball cover compositions and the resulting multi-layer golf balls produced using the improved compositions. The novel multi-layer golf ball covers of the present invention include a first or inner layer or ply of a high acid (greater than 16 weight percent acid) ionomer blend or, more preferably, a low acid (16 weight percent acid or less) ionomer blend and second or outer layer or ply comprised of a comparatively softer, low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane or polyester elastomer. The multi-layer golf balls of the invention can be of standard or enlarged size. Preferably, the inner layer or ply incudes a blend of low acid ionomers and has a Shore D hardness of 60 or greater and the outer cover layer comprised of polyurethane and has a Shore D hardness of about 45 (i.e., Shore C hardness of about 65).

It has been found that multi-layer golf balls having inner and outer cover layers exhibit higher C.O.R. values and have greater travel distance in comparison with balls made from a single cover layer. In addition, it has been found that use of a inner cover layer constructed of a blend of low acid (i.e., 16 weight percent acid or less) ionomer resins produces softer compression and higher spin rates than inner cover layers constructed of high acid ionomer resins. This is compounded by the fact that the softer polyurethane outer layer adds to the desirable "feel" and high spin rate while maintaining respectable resiliency. The soft outer layer allows the cover to deform more during impact and increases the area of contact between the club face and the cover, thereby imparting more spin on the ball. As a result, the soft polyurethane cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability.

Consequently, the overall combination of inner and outer cover layers made from blends of low acid ionomer resins and polyurethane results in a standard size or oversized golf ball having enhanced resilience (improved travel distance) and durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the balls playability properties.

The combination of a low acid ionomer blend inner cover layer with a soft, relatively low modulus ionomer, polyurethane based elastomer outer cover layer provides for good overall coefficient of restitution (i.e., enhanced resilience) while at the same time demonstrating improved compression and spin. The outer cover layer generally contributes to a more desirable feel and spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Resilience (C.O.R.), along with additional factors such as club head speed, angle of trajectory and ball configuration (i.e., dimple pattern) generally determine the distance a ball will travel when hit. Since club head speed and the angle of trajectory are factors not easily controllable by a manufacturer, factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

The coefficient of restitution (C.O.R.) in solid core balls is a function of the composition of the molded core and of the cover. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings. Although both the core and the cover contribute to the coefficient of restitution, the present invention is directed to the enhanced coefficient of restitution (and thus travel distance) which is affected by the cover components.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and measuring the ball's incoming and outgoing velocity electronically. As mentioned above, the coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States Golf Association (U.S.G.A.). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by

the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Pat. No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests such as the "nine iron" spin rate test described below in the Examples

Accordingly, the present invention is directed to an improved multi-layer cover which produces, upon molding each layer around a core (preferably a solid core) to formulate a multi-layer cover, a golf ball exhibiting enhanced distance (i.e., resilience) without adversely affecting, and in many instances, improving the ball's playability (hardness/softness) and/or durability (i.e., cut resistance, fatigue resistance, etc.) characteristics.

These and other objects and features of the invention will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional view of a golf ball embodying the invention illustrating a core **10** and a cover **12** consisting of an inner layer **14** and an outer layer **16** having dimples **18**; and

FIG. **2** is a diametrical cross-sectional view of a golf ball of the invention having a core **10** and a cover **12** made of an inner layer **14** and an outer layer **16** having dimple **18**.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to improved multi-layer golf balls, particularly a golf ball comprising a multi-layered cover **12** over a solid core **10**, and method for making same.

The multi-layered cover **12** comprises two layers: a first or inner layer or ply **14** and a second or outer layer or ply **16**. The inner layer **14** is comprised of a low acid (i.e. 16 weight percent acid or less) ionomer blend. Preferably, the inner layer is comprised of a blend of two or more low acid (i.e. 16 weight percent acid or less) ionomer resins neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

The low acid ionomers which may be suitable for use in formulating the inner layer compositions of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10–75%, preferably 30–70%) by the metal ions. Each of the low acid ionomer resins which may be included in the inner layer cover compositions of the invention contains 16% by weight or less of a carboxylic acid.

The inner layer compositions include the low acid ionomers such as those developed and sold by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or tradename "Iotek", or blends thereof.

The low acid ionomeric resins available from Exxon under the designation "Escort" and or "Iotek", are somewhat similar to the low acid ionomeric resins available under the "Surlyn®" trademark. However, since the Escor®/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the "Surlyn®" resins are zinc, sodium, magnesium,—etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the low acid ionomer blends extend the range of compression and spin rates beyond that previously obtainable. More preferably, it has been found that when two or more low acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further and at an enhanced spin rate than previously known multi-layered golf balls. Such an improvement is particularly noticeable in enlarged or oversized golf balls.

For example, the normal size, multi-layer golf ball taught in U.S. Pat. No. 4,650,193 does not incorporate blends of low acid ionomeric resins of the present invention in the inner cover layer. In addition, the multi-layered ball disclosed in the '193 patent suffers substantially in durability in comparison with the present invention.

Furthermore, as shown in the Examples, use of a inner layer formulated from blends of lower acid ionomers produces multi-layer golf balls having enhanced compression and spin rates. These are the properties desired by the more skilled golfer.

With respect to the outer layer **16** of the multi-layered cover of the present invention, the outer cover layer is comparatively softer than the low acid ionomer blend based inner layer. The softness provides for the enhanced feel and playability characteristics typically associated with balata or balata-blend balls. The outer layer or ply is comprised of a relatively soft, low modulus (about 1,000 psi to about 10,000 psi) and low acid (less than 16 weight percent acid) ionomer, ionomer blend or a non-ionomeric elastomer such as, but not limited to, a polyurethane, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, a polyurethane sold by BASF under the designation Baytec® or a polyester amide such as that marketed by Elf Atochem S. A. under the trademark Pebax®. The outer layer is fairly thin (i.e. from about 0.010 to about 0.070 in thickness, more desirably 0.03 to 0.06 inches in thickness for a 1.680 inch ball and 0.04 to 0.07 inches in thickness for a 1.72 inch ball),

but thick enough to achieve desired playability characteristics while minimizing expense.

Preferably, the outer layer includes a blend of hard and soft (low acid) ionomer resins such as those described in U.S. Pat. Nos. 4,884,814 and 5,120,791, both incorporated herein by reference. Specifically, a desirable material for use in molding the outer layer comprises a blend of a high modulus (hard), low acid, ionomer with a low modulus (soft), low acid, ionomer to form a base ionomer mixture. A high modulus ionomer herein is one which measures from about 15,000 to about 70,000 psi as measured in accordance with ASTM method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240.

A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale.

The hard ionomer resins utilized to produce the outer cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium or lithium salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15–75 percent) neutralized.

The hard ionomeric resins are likely copolymers of ethylene and either acrylic and/or methacrylic acid, with

since the "Iotek" ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of poly(ethylene-methacrylic acid) some distinct differences in properties exist. As more specifically indicated—in the data set forth below, the hard "Iotek" resins (i.e., the acrylic acid based hard ionomer resins) are the more preferred hard resins for use in formulating the outer layer blends for use in the present invention. In addition, various blends of "Iotek" and Surlyn® hard ionomeric resins, as well as other available ionomeric resins, may be utilized in the present invention in a similar manner.

Examples of commercially available hard ionomeric resins which may be used in the present invention in formulating the inner and outer cover blends include the hard sodium ionic copolymer sold under the trademark Surlyn®8940 and the hard zinc ionic copolymer sold under the trademark Surlyn®9910. Surlyn®8940 is a copolymer of ethylene with methacrylic acid and about 15 weight percent acid which is about 29 percent neutralized with sodium ions. This resin has an average melt flow index of about 2.8. Surlyn®9910 is a copolymer of ethylene and methacrylic acid with about 15 weight percent acid which is about 58 percent neutralized with zinc ions. The average melt flow index of Surlyn®9910 is about 0.7. The is typical properties of Surlyn®9910 and 8940 are set forth below in Table 1:

TABLE 1

Typical Properties of Commercially Available Hard Surlyn ® Resins Suitable for Use in the Inner and Outer Layer Blends of the Present Invention

	ASTM D	8940	9910	8920	8528	9970	9730
Cation Type		Sodium	Zinc	Sodium	Sodium	Zinc	Zinc
Melt flow index, gms/10 min.	D-1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, g/cm^3	D-792	0.95	0.97	0.95	0.94	0.95	0.95
Hardness Shore D	D-2240	66	64	66	60	62	63
Tensile Strength, (kpsi), MPa	D-638	(4.8) 33.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(4.1) 28.0
Elongation, %	D-638	470	290	350	450	460	460
Flexural Modulus, (kpsi) MPa	D-790	(51) 350	(48) 330	(55) 380	(32) 220	(28) 190	(30) 210
Tensile Impact (23° C.) KJ/m$_2$ (ft.-lbs./in^2)	D-1822S	1020 (485)	1020 (485)	865 (410)	1160 (550)	760 (360)	1240 (590)
Vicat Temperature, ° C.	D-1525	63	62	58	73	61	73

copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

As discussed earlier herein, the hard ionomeric resins introduced under the designation Escor® and sold under the designation "Iotek" are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However,

Examples of the more pertinent acrylic acid based hard ionomer resin suitable for use in the present inner and outer cover composition sold under the "Iotek" tradename by the Exxon Corporation include Iotek 4000, Iotek 4010, Iotek 8000, Iotek 8020 and Iotek 8030. The typical properties of these and other Iotek hard ionomers suited for use in formulating the inner and outer is layer cover compositions are set forth below in Table 2:

TABLE 2

Typical Properties of Iotek Ionomers

Resin Properties	ASTM Method	Units	4000	4010	8000	8020	8030
Cation type			zinc	zinc	sodium	sodium	sodium
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6	2.8
Density	D-1505	kg/m^3	963	963	954	960	960
Melting Point	D-3417	° C.	90	90	90	87.5	87.5
Crystallization Point	D-3417	° C.	62	64	56	53	55
Vicat Softening Point	D-1525	° C.	62	63	61	64	67
% Weight Acrylic Acid			16		11		
% of Acid Groups cation neutralized			30		40		
Plaque Properties (3 mm thick, compression molded)							
Tensile at break	D-638	MPa	24	26	36	31.5	28
Yield point	D-638	MPa	none	none	21	21	23
Elongation at break	D-638	%	395	420	350	410	395
1% Secant modulus	D-638	MPa	160	160	300	350	390
Shore Hardness D	D-2240	—	55	55	61	58	59
Film Properties (50 micron film 2.2:1 Blow-up ratio)							
Tensile at Break MD	D-882	MPa	41	39	42	52	47.4
TD	D-882	MPa	37	38	38	38	40.5
Yield point MD	D-882	MPa	15	17	17	23	21.6
TD	D-882	MPa	14	15	15	21	20.7
Elongation at Break							
MD	D-882	%	310	270	260	295	305
TD	D-882	%	360	340	280	340	345
1% Secant modulus MD	D-882	MPa	210	215	390	380	380
TD	D-882	MPa	200	225	380	350	345
Dart Drop Impact	D-1709	g/micron	12.4	12.5	20.3		

Resin Properties	ASTM Method	Units	7010	7020	7030
Cation type			zinc	zinc	zinc
Melt Index	D-1238	g/10 min	0.8	1.5	2.5
Density	D-1505	kg/m^3	960	960	960
Melting Point	D-3417	° C.	90	90	90
Crystallization Point	D-3417	° C.	—	—	—
Vicat Softening Point	D-1525	° C.	60	63	62.5
% Weight Acrylic Acid			—	—	—
% of Acid Groups Cation Neutralized			—	—	—
Plaque Properties (3 mm thick, compression molded)					
Tensile at break	D-638	MPa	38	38	38
Yield Point	D-638	MPa	none	none	none
Elongation at break	D-638	%	500	420	395
1% Secant modulus	D-638	MPa	—	—	—
Shore Hardness D	D-2240	—	57	55	55

Comparatively, soft ionomers are used in formulating the hard/soft blends of the inner and outer cover compositions. These ionomers include acrylic acid based soft ionomers. They are generally characterized as comprising sodium or zinc salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, acrylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably a zinc based ionomer made from an acrylic acid base polymer in an unsaturated monomer of the acrylate ester class. The soft (low modulus) ionomers have a hardness from about 20 to about 40 as measured on the Shore D scale and a flexural modulus from about 1,000 to about 10,000, as measured in accordance with ASTM method D-790.

Certain ethylene-acrylic acid based soft ionomer resins developed by the Exxon Corporation under the designation "Iotek 7520" (referred to experimentally by differences in neutralization and melt indexes as LDX 195, LDX 196, LDX 218 and LDX 219) may be combined with known hard ionomers such as those indicated above to produce the inner and outer cover layers. The combination produces higher C.O.R.s at equal or softer hardness, higher melt flow (which

corresponds to improved, more efficient molding, i.e., fewer rejects) as well as significant cost savings versus the inner and outer layers of multi-layer balls produced by other known hard-soft ionomer blends as a result of the lower overall raw materials costs and improved yields.

While the exact chemical composition of the resins to be sold by Exxon under the designation Iotek 7520 is considered by Exxon to be confidential and proprietary information, Exxon's experimental product data sheet lists the following physical properties of the ethylene acrylic acid zinc ionomer developed by Exxon:

TABLE 3

Physical Properties of Iotek 7520			
Property	ASTM Method	Units	Typical Value
Melt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m^3	0.962
Cation			Zinc
Melting Point	D-3417	° C.	66
Crystallization Point	D-3417	° C.	49
Vicat Softening Point	D-1525	° C.	42
Plague Properties (2 mm thick Compression Molded Plaques)			
Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	None
Elongation at Break	D-638	%	760
1% Secant Modulus	D-638	MPa	22
Shore D Hardness	D-2240		32
Flexural Modulus	D-790	MPa	26
Zwick Rebond	ISO 4862	%	52
De Mattia Flex Resistance	D-430	Cycles	>5000

In addition, test data collected by the inventor indicates that Iotek 7520 resins have Shore D hardnesses of about 32 to 36 (per ASTM D-2240), melt flow indexes of 3±0.5 g/10 min (at 190° C. per ASTM D-1288), and a flexural modulus of about 2500–3500 psi (per ASTM D-790). Furthermore, testing by an independent testing laboratory by pyrolysis mass spectrometry indicates that Iotek 7520 resins are generally zinc salts of a terpolymer of ethylene, acrylic acid, and methyl acrylate.

Furthermore, the inventor has found that a newly developed grade of an acrylic acid based soft ionomer available from the Exxon Corporation under the designation Iotek 7510, is also effective, when combined with the hard ionomers indicated above in producing golf ball covers exhibiting higher C.O.R. values at equal or softer hardness than those produced by known hard-soft ionomer blends. In this regard, Iotek 7510 has the advantages (i.e. improved flow, higher C.O.R. values at equal hardness, increased clarity, etc.) produced by the Iotek 7520 resin when compared to the methacrylic acid base soft ionomers known in the art (such as the Surlyn 8625 and the Surlyn 8629 combinations disclosed in U.S. Pat. No. 4,884,814).

In addition, Iotek 7510, when compared to Iotek 7520, produces slightly higher C.O.R. valves at equal softness/hardness due to the Iotek 7510's higher hardness and neutralization. Similarly, Iotek 7510 produces better release properties (from the mold cavities) due to its slightly higher stiffness and lower flow rate than Iotek 7520. This is important in production where the soft covered balls tend to have lower yields caused by sticking in the molds and subsequent punched pin marks from the knockouts.

According to Exxon, Iotek 7510 is of similar chemical composition as Iotek 7520 (i.e. a zinc salt of a terpolymer of

ethylene, acrylic acid, and methyl acrylate) but is more highly neutralized. Based upon FTIR analysis, Iotek 7520 is estimated to be about 30–40 wt.-% neutralized and Iotek 7510 is estimated to be about 40–60 wt.-% neutralized. The typical properties of Iotek 7510 in comparison of those of Iotek 7520 are set forth below:

TABLE 4

Physical Properties of Iotek 7510 in Comparison to Iotek 7520	IOTEK 7520	IOTEK 7510
MI, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Melting Point, ° F.	151	149
Vicat Softening Point, ° F.	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

It has been determined that when hard/soft ionomer blends are used for the outer cover layer, good results are achieved when the relative combination is in a range of about 90 to about 10 percent hard ionomer and about 10 to about 90 percent soft ionomer. The results are improved by adjusting the range to about 75 to 25 percent hard ionomer and 25 to 75 percent soft ionomer. Even better results are noted at relative ranges of about 60 to 90 percent hard ionomer resin and about 40 to 60 percent soft ionomer resin.

Specific formulations which may be used in the cover composition are included in the examples set forth in U.S. Pat. Nos. 5,120,791 and 4,884,814. The present invention is in no way limited to those examples.

Moreover, in alternative embodiments, the outer cover layer formulation may also comprise a soft, low modulus, non-ionomeric thermoplastic elastomer having a flex modulus in a range of about 1,000 to about 30,000 psi, including a polyester polyurethane such as B. F. Goodrich Company's Estane® polyester polyurethane X-4517. According to B. F. Goodrich, Estane® X-4517 has the following properties:

Properties of Estane ® X-4517	
Tensile	1430
100%	815
200%	1024
300%	1193
Elongation	641
Youngs Modulus	1826
Hardness A/D	88/39
Dayshore Rebound	59
Solubility in Water	Insoluble
Melt processing temperature	>350° F. (>177° C.)
Specific Gravity (H_2O = 1)	1.1–1.3

Other soft, relatively low modulus non-ionomeric thermoplastic elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced spin characteristics produced by the low acid iouomer resin compositions. Preferably, the non-ionomeric thermoplastic elastomers have a Shore D hardness of 64 or less. These include, but are not limited to thermoplastic polyurethanes such as: Texin® thermoplastic polyurethanes from Mobay Chemical Co. and the Pellethane® thermoplastic polyure-

thanes from Dow Chemical Co.; Ionomer/rubber blends such as those in Spalding U.S. Pat. Nos. 4,986,545; 5,098,105 and 5,187,013; and, Hytrel® polyester elastomers from DuPont and Pebax® polyetheramides from Elf Atochem S. A.

Similarly, a castable, thermosetting polyurethane produced by BASF under the trade designation Baytec® has also shown enhanced cover formulation properties. According to BASF, Baytec® (such as Baytec® RE 832), relates to a group of reactive elastomers having outstanding wear resistance, high mechanical strength, high elasticity and good resistance to weathering, moisture and chemicals. The Baytec® RE-832 system gives the following typical physical properties:

Property	ASTM Test Method	Unit	Value
Tear Strength Die C	D624	pli	180
Stress at			
100% Modulus	D412	psi	320
200% Modulus			460
300% Modulus			600
Ultimate Strength	D412	psi	900
Elongation at Break	D412	%	490
Taber Abrasion	D460, H-18	mg/1000 cycles	350

Component[1] Properties	Part A (Isocyanate)	Part B (Resin)
Viscosity @ 25° C., mPa · s	2500	2100
Density @ 25° C., g/cm	1.08	1.09
NCO, %	9.80	—
Hydroxyl Number, Mg KOH/g	—	88

[1]Component A is a modified diphenylmethane diisocyanate (mDI) prepolymer and component B is a polyether polyol blend.

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core). A comparatively softer outer layer is molded over the inner layer.

The conventional solid core is about 1.545 inches in diameter, although it can range from about 1.495 to about 1.575 inches. Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an α, β, ethylenically unsaturated carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include fillers such as small amounts of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the desired coefficient are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiators such as peroxides are admixed with the core composition so that on the application of heat and pressure, a complex curing cross-linking reaction takes place.

The inner cover layer which is molded over the core is about 0.100 inches to about 0.010 inches in thickness, preferably about 0.0375 inches thick. The outer cover layer is about 0.010 inches to about 0.050 inches in thickness, preferably 0.0300 inches thick. Together, the core, the inner cover layer and the outer cover layer combine to form a ball having a diameter of 1.680 inches or more, the minimum diameter permitted by the rules of the United States Golf Association and weighing about 1.620 ounces.

Additional materials may be added to the cover compositions (both inner and outer cover layer) of the present invention including dyes (for example, Ultramarine Blue sold by Whitaker, Clark and Daniels of South Plainsfield, N.J.) (see U.S. Pat. No. 4,679,795); pigments such as titanium dioxide, zinc oxide, barium sulfate and zinc sulfate; and UV absorbers; antioxidants; antistatic agents; and stabilizers. Further, the cover compositions of the present invention may also contain softening agents, such as plasticizers, processing aide, etc. and reinforcing material such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers are not impaired.

The various cover composition layers of the present invention may be produced according to conventional melt blending procedures. In the case of the outer cover layer, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the desired additives in a Banbury mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the low acid ionomer resin compositions used to produce the inner cover layer.

The golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the inner cover layer about wound or solid molded cores to produce an intermediate golf ball having a diameter of about 1.50 to 1.67 inches, preferably about 1.620 inches. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.680 inches or more. Although either solid cores or wound cores can be used in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound cores.

In compression molding, the inner cover composition is formed via injection at about 380° F. to about 450° F. into smooth surfaced hemispherical shells which are then positioned around the core in a mold having the desired inner cover thickness and subjected to compression molding at 200° to 300° F. for about 2 to 10 minutes, followed by cooling at 50° to 70° F. for about 2 to 7 minutes to fuse the shells together to form a unitary intermediate ball. In addition, the intermediate balls may be produced by injection molding wherein the inner cover layer is injected directly around the core placed at the center of an intermediate ball mold for a period of time in a mold temperature of from 50° F. to about 100° F. Subsequently, the outer cover layer is molded about the core and the inner layer by similar compression or injection molding techniques to form a dimpled golf ball of a diameter of 1.680 inches or more.

After molding, the golf balls produced may undergo various further processing steps such as buffing, painting and marking as disclosed in U.S. Pat. No. 4,911,451.

The resulting golf ball produced from the low acid ionomer resin inner layer and the relatively softer, low flexural modulus outer layer provide for an improved multi-layer golf ball which proyides for desirable coefficient of restitution, compression, spin and durability properties while at the same time offering the feel characteristics associated with soft balata and balata-like covers of the prior art.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

EXAMPLE 1

Several intermediate balls (cores plus inner cover layers) were prepared in accordance with conventional molding procedures described above. The inner cover compositions were molded around 1.545 inch diameter cores weighing 36.5 grams such that the inner cover had a wall thickness of about 0.0675 inches, with the overall ball measuring about 1.680 inches in diameter.

The cores utilized in the examples were comprised of the following ingredients: high cis-polybutadiene, zinc diacrylate, zinc oxide, zinc stearate, peroxide, calcium carbonate, etc. The molded cores exhibited Riehle compressions of about 60 and C.O.R. values of about 0.800. A representative formulation of the molded cores is set forth below:

MATERIAL	WEIGHT
BR-1220 (high cis-polybutadiene)	70.70
Taktene 220 (high cis-polybutadiene)	29.30
React Rite ZDA (zinc diacrylate)	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash (20–40 Mesh)	20.15
Blue Masterbatch	.012
Luperco 231XL or Trigonax 29/40	.89
Papi 94	.50

[1]Blue Masterbatch consists of unknown compositions used only for internal identification purposes and has no effect on physical properties.

The inner cover compositions designated herein as compositions A–E utilized to formulate the intermediate balls are set forth in Table 7 below The resulting molded intermediate balls were tested to determine the individual compression

(Riehle), C.O.R., Shore C hardness, spin rate and cut resistance properties. These results are also set forth in Table 7 below.

The data of these examples are the average of twelve intermediate balls produced for each example The properties were measured according to the following parameters:

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air canon at a velocity of 125 feet per second against a steel plate positioned 12 feet from the muzzle of the canon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give a coefficient of restitution.

Shore hardness was measured in accordance with ASTM test 2240.

Cut resistance was measured in accordance with the following procedure: A golf ball is fired at 135 feet per second against the leading edge of a pitching wedge wherein the leading edge radius is 1/32 inch, the loft angle is 51 degrees, the sole radius is 2.5 inches and the bounce angle is 7 degrees.

The cut resistance of the balls tested herein was evaluated on a scale of 1 to 5. The number 1 represents a cut that extends completely through the cover to the core. A 2 represents a cut that does not extend completely through the cover but that does break the surface. A 3 does not break the surface of the cover but does leave a permanent dent. A 4 leaves only a slight crease which is permanent but not as severe as 3. A 5 represents virtually no visible indentation or damage of any sort.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9 iron wherein the club head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110 to 115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

Initial velocity is the velocity of a ball when struck at a hammer speed of 143.8 feet per second in accordance with a test as prescribed by the U.S.G.A.

As will be noted, compositions A, B and C include high acid ionomeric resins (16% or more acid), with composition B further including zinc stearate. Composition D represents the inner layer (i.e. Surlyn 1605) used in U.S. Pat. No. 4,431,193. Composition E provides a hard, low acid ionomeric resin blend.

The purpose behind producing and testing the balls of Table 5 was to provide a subsequent comparison in properties with the multi-layer golf balls of the present invention.

TABLE 5

Molded Intermediate Golf Balls

Ingredients of Inner Cover Compositions	A	B	C	D	E
Iotek 959	50	50	—	—	—
Iotek 960	50	50	—	—	—
Zinc Stearate	—	50	—	—	—
Surlyn 8162	—	—	75	—	—
Surlyn 8422	—	—	25	—	—
Surlyn 1605	—	—	—	100	—
Iotek 7030	—	—	—	—	50
Iotek 8000	—	—	—	—	50

TABLE 5-continued

Ingredients of Inner Cover Compositions	Molded Intermediate Golf Balls A	B	C	D	E
Properties of Molded Intermediate Balls					
Compression	58	58	60	63	62
C.O.R.	.811	.810	.807	.793	.801
Shore C Hardness	98	98	97	96	96
Spin Rate (R.P.M.)	7,367	6,250	7,903	8,337	7,956
Cut Resistance	4–5	4–5	4–5	4–5	4–5

As shown in Table 5 above, the high acid ionomer resin inner cover layer (molded intermediate balls A–C) have lower spin rates and exhibit higher resiliency characteristics than the low acid ionomer resin based inner cover layers of balls D and E.

Multi-layer balls in accordance with the present invention were then prepared. Specifically, the inner cover compositions used to produce intermediate golf balls from Table 5 were molded over the solid cores to a thickness of about 0.0375 inches, thus forming the inner layer. The diameter of the solid core with the inner layer measured about 1.620 inches. Alternatively, the intermediate golf balls of Table 5 were ground down using a centerless grinding machine to a size of 1.620 inches in diameter to produce an inner cover layer of 0.0375 inches.

The size of 1.620 inches was determined after attempting to mold the outer cover layer to various sizes (1.600", 1.610", 1.620", 1.630" and 1.640") of intermediate (core plus inner layer) balls. It was determined that 1.620" was about the largest "intermediate" ball (i.e., core plus inner layer) which could be easily molded over with the soft outer layer materials of choice. The goal herein was to use as thin an outer layer as necessary to achieve the desired playability characteristics while minimizing the cost of the more expensive outer materials. However, with a larger diameter final golf ball and/or if the cover is compression molded, a thinner cover becomes feasible.

With the above in mind, an outer cover layer composition was blended together in accordance with conventional blending techniques. The outer layer composition used for this portion of the example is a relatively soft cover composition such as those listed in U.S. Pat. No. 5,120,791. An example of such a soft cover composition is a 45% soft/55% hard low acid ionomer blend designated by the inventor as "TE-90". The composition of TE-90 is set forth as follows:

Outer Cover Layer Composition TE-90	
Iotek 8000	22.7 weight %
Iotek 7030	22.7 weight %
Iotek 7520	45.0 weight %
White MB[1]	9.6 weight %

[1]White MB consists of about 23.77 weight percent TiO_2; 0.22 weight percent Uvitex OB, 0.03 weight percent Santonox R, 0.05 weight percent Ultramarine blue and 75.85 weight percent Iotek 7030.

The above outer layer composition was molded around each of the 1.620 diameter intermediate balls comprising a core plus one of compositions A–D, respectively. In addition, for comparison purposes, Surlyn® 1855 (new Surlyn® 9020), the cover composition of the '193 patent, was molded about the inner layer of composition D (the intermediate ball representative of the '193 patent). The outer layer TE-90 was molded to a thickness of approximately 0.030 inches to produce a golf ball of approximately 1.680 inches in diameter. The resulting balls (a dozen balls for each example) were tested and the various properties thereof are set forth in Table 6A as follows:

TABLE 6A

Ingredients:	Finished Balls 1	2	3	4	5
Inner Cover Composition	A	B	C	D	D
Outer Cover Composition	TE-90	TE-90	TE-90	TE-90	Surlyn ® 9020
Properties of Molded Finished Balls:					
Compression	63	63	69	70	61
C.O.R.	.784	.778	.780	.770	.757
Shore C Hardness	88	88	88	88	89
Spin (R.P.M.)	8,825	8,854	8,814	8,990	8,846
Cut Resistance	3–4	3–4	3–4	3–4	1–2

As it will be noted in finished balls 1–4, by creating a multi-layer cover utilizing the high acid ionomer resins in the inner cover layer and the hard/soft low acid ionomer resins in the outer cover layer, higher compression and increased spin rates are noted over the single layer covers of Table 5. In addition, both the C.O.R. and the Shore C hardness are reduced over the respective single layer covers of Table 5. This was once again particularly true with respect to the multi-layered balls containing the high acid ionomer resin in the inner layer (i.e. finished balls 1–4). In addition, with the exception of prior art ball 5 (i.e. the '193 patent), resistance to cutting remains good but is slightly decreased.

As noted above, the prior art ball of the '193 patent suffers substantially in durability (as well as in resiliency) in comparison to the balls of the invention.

Furthermore, it is also noted that the use of the high acid ionomer resins as the inner cover material produces a substantial increase in the finished balls overall distance properties. In this regard, the high acid ionomer resin inner covers of balls 1–3 produce an increase of approximately 10 points in C.O.R. over the low acid ionomer resin inner covers of balls 4 and about a 25 point increase over the prior art balls 5. Since an increase in 3 to 6 points in C.O.R. results in an average increase of about 1 yard in distance, such an improvement is deemed to be significant.

Several other outer layer formulations were prepared and tested by molding them around the core and inner cover layer combination to form balls each having a diameter of about 1.68 inches. First, B. F. Goodrich Estane® X-4517 polyester polyurethane was molded about the core molded with inner layer cover formulation A. DuPont Surlyn® 9020 was molded about the core which was already molded with inner layer D. Similar properties tests were conducted on these golf balls and the results are set forth in Table 6B below:

TABLE 6B

Ingredients:	Finish Balls 6	Finish Balls 7
Inner Cover Layer Composition	A	D
Outer Cover Layer Composition	Estane ® 4517	Surlyn ® 9020
Properties of Molded Finished Balls:		
Compression	67	61
C.O.R.	.774	.757
Shore C Hardness	74	89
Spin (R.P.M.)	10,061	8,846
Cut Resistance	3–4	1–2

The ball comprising inner layer formulation D and Surlyn® 9020 identifies the ball in the Nesbitt 4,431,193 patent. As is noted, the example provides for relatively high softness and spin rate though it suffers from poor cut resistance and low C.O.R. This ball is unacceptable by today's standards.

As for the Estane® X-4517 polyester polyurethane, a significant increase in spin rate over the TE-90 cover is noted along with an increased compression. However, the C.O.R. and Shore C values are reduced, while the cut resistance remains the same. Furthermore, both the Estane® X-4517 polyester polyurethane and the Surlyn® 9020 were relatively difficult to mold in such thin sections.

EXAMPLE 2

In order to analyze the change in characteristics produced by multi-layer golf balls (standard size) having inner cover layers comprised of ionomer resin blends of different acid levels, a series of experiments were run. Specifically, 14 tests were performed, varying the type of core, inner cover layer and outer cover layer. The results are shown below:

TABLE 7

Sample #	CORE	INNER LAYER	THICKNESS	COMP/ COR	OUTER COVER	THICKNESS	COMP (Rhiele)	COR	SHORE D	SPIN
8	1042 YELLOW	NONE	—	SEE BELOW	TOP GRADE	0.055"	61	.800	68	7331
9	1042 YELLOW	NONE	—	SEE BELOW	959/960	0.055"	56	.808	73	6516
10	SPECIAL 1.47"	959/960	0.050"	65/.805	959/960	0.055"	48	.830	73	6258
11	1042 YELLOW	NONE	—	SEE BELOW	SD 90	0.055"	62	.792	63	8421
12	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	SD 90	0.055"	55	.811	63	8265
13	SPECIAL 1.47"	959/960	0.050"	65/.805	SD 90	0.055"	53	.813	63	8254
14	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	TOP GRADE	0.055"	51	.819	68	7390
15	1042 YELLOW	NONE	—	SEE BELOW	Z-BALATA	0.055"	67	.782	55	9479
16	SPECIAL 1.47"	959/960	0.050"	65/.805	Z-BALATA	0.055"	61	.800	55	9026
17	SPECIAL 1.47"	TOP GRADE	0.050"	66/.799	Z-BALATA	0.055"	60	.798	55	9262

1042 YELLOW > COMP = 72, COR = .780
SPECIAL 1.47" CORE > COMP = 67, COR = .782

In this regard, "Top Grade" or "TG" is a low acid inner cover ionomer resin blend comprising of 70.6% Iotek 8000, 19.9% Iotek 7010 and 9.6% white masterbatch. "959/960" is a 50/50 wt/wt blend of Iotek 959/960. In this regard, Escor® or Iotek 959 is a sodium ion neutralized ethylene-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

PROPERTY	ESCOR ® (IOTEK) 959	ESCOR ® (IOTEK) 960
Melt Index g/10 min	2.0	1.8
Cation	Sodium	Zinc
Melting Point, ° F.	172	174
Vicat Softening Point, ° F.	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, the low acid ionomer formulation for "SD 90" and "Z-Balata" are set forth below:

SD Cover	ZB Cover
17.2% Surlyn 8320	19% Iotek 8000
7.5% Surlyn 8120	19% Iotek 7030
49% Surlyn 9910	52.5% Iotek 7520
16.4% Surlyn 8940	95% white MB
9.7% white MB	

The data clearly indicates that higher C.O.R. and hence increase travel distance can be obtained by using multi-layered covered balls versus balls covered with single layers. However, some sacrifices in compression and spin are also noted. Further, as shown in comparing Example Nos. 12 vs. 13, Example Nos. 17 vs. 16, etc., use of lower acid level inner cover layers and relatively soft outer cover layers (i.e., 50 wt. % or more soft ionomer) produces softer compression and higher spin rates than the golf balls comprised of high acid inner cover layers. Consequently, use of blends of low acid ionomer resins to produce the inner layer of a multi-layer covered golf ball, produces not only enhanced travel distance but also enhanced compression and spin properties.

EXAMPLE 3

Multi-layer oversized golf balls were produced utilizing different ionomer resin blends as the inner cover layer (i.e., core plus inner cover layer is defined as "mantel"). The "ball data" of the oversized multi-layer golf balls in comparison with production samples of "Top-Flite® XL" and "Top-Flite® Z-Balata" is set forth below.

TABLE 8

	18	19	20	21 Top-Flite ® XL	22 Top-Flite ® Z-Balata 90
Core Data					
Size	1.43	1.43	1.43	1.545	1.545
COR	.787	.787	.787	—	—
Mantel Date					
Material	TG	TG	TG	—	—
Size	.161	1.61	1.61	—	—
Thickness	.090	.090	.090	—	—
Shore D	68	68	68	—	—
Compression	57	57	57	—	—
COR	.815	.815	.815	—	—
Ball Data					
Cover	TG	ZB	SD	TG	ZB
Size	1.725	1.723	1.726	1.681	1.683
Weight	45.2	45.1	45.2	45.3	45.5
Shore D	68	56	63	68	56
Compression	45	55	49	53	77

TABLE 8-continued

	18	19	20	21 Top-Flite ® XL	22 Top-Flite ® Z-Balata 90
COR	.820	.800	.810	.809	.797
Spin	7230	9268	8397	7133	9287

The results indicate that use of multi-layer covers enhances C.O.R. and travel distance. Further, the data shows that use of a blend of low acid ionomer resins (i.e., "Top Grade") to form the inner cover layer in combination with a soft outer cover ("ZB" or "SD") produces enhanced spin and compression characteristics. The overall combination results in a relatively optimal golf ball with respect to characteristics of travel distances, spin and durability.

EXAMPLE 4

Castable Polyurethane Covered Multi-layer Balls

A limited number of samples were made using BASF Baytec® RE232 polyurethane as a cover material over four different types of mantle cores. Controls included Z-Balata 100s along with the same mantle cores used for the polyurethane samples covered with Z-Balata cover stock Mantle cores were made up of 82 and 58 compression cores covered with Iotek 8030/7030.

Castable PU Molding Process
Materials used:
Baytec ® RE832, mix ratio 9 parts A/12 parts B
1 - 1.57" i.d. smooth cavity
2 - 1.68" i.d. dimpled cavities
1 - 2" hose clamp
1 - bench vise or large C-clamp

(The smooth and dimpled cavities are the same O.D.)

The mantle core is 1.57" and fits snugly in the 1.57" cavity. The hose clamp is attached to the 1.57" cavity and a mantle core is placed in inside. Urethane is mixed and poured into one of the dimpled cavities and the two halves are placed together and clamped, forcing out excess material and forming half the cover. The hose clamp in used to keep the two mold halves aligned during curing. When the cover material is set up enough (about 5 minutes), the two halves are separated and the 1.57" mold is replaced with the other 1.68" mold and the process is repeated. Both halves of the cover are now cast and the entire assemble is placed in an 125f oven for 1 hour after which it can be opened and the ball removed.

All samples were finished using normal production equipment and procedures. The properties of the finished balls are set forth below:

TABLE 9

	23	23	24	25	26	27	28	29
CORE DATA								
Size	1.47"	1.47"	1.47"	1.47"	1.47"	1.47"	1.47"	1.47"
Weight	32.2	32	32.2	32	37.7	32.2	32	32.2

TABLE 9-continued

	23	23	24	25	26	27	28	29
Comp	82	58	82	58	85	82	58	82
COR	768	772	768	772	794	768	772	768
MANTLE DATA	Iotek	Iotek	Iotek	Iotek		Iotek	Iotek	Iotek
Material	8030/7030	8030/7030	8030/7030	8030/7030	None	8030/7030	8030/7030	8030/7030
Weight	37.8	38.1	37.9	38.1		37.8	38.1	37.9
Size	1.57"	1.57"	1.57"	1.57"		1.57"	1.57"	1.57"
Comp	70	48	69	48		70	48	69
COR	781	785	786	788		781	785	786
BALL DATA								
Cover Material	Baytec RE832	Baytec RE832	Baytec RE832	Baytec RE832	Z-Balata	Z-Balata	Z-Balata	Z-Balata
Weight	45.4	45.5	45.5	45.2	45.3	44.8	45	
Comp	75	64	73	60	80	66	50	65
COR	771	763	770	761	792	775	774	778
Shore C	65	65	65	65	84	84	84	84
Spin (rpm)	9560	8789	9285	8760	8796	8702	9072	8643
Cut (1-good, 4-poor)	2	2	2	1.5	2	2	2	2
Scuff (1-good, 4-poor)	1.5	1.5	1.5	1.5	2	3	3	3

Table 9 contains the construction details and test results Multilayer balls with the thermoset urethane covers (Examples 23–25) were softer in compression and similar in COR to the multi-layer balls with the Z-Balata cover (Examples 27–29). shore C was much lower for the urethane balls and they were more resistant to scuff than any of the Z-Balata covered balls. Guillotine cut resistance was about the same. Spin rate comparison shows that the urethane samples are better than the Z-Balata covered balls.

Test results indicate that a very good multi-layer ball can be made using castable polyurethane cover material. Further, advantages include the molding very thin covers, molding over very soft compression core/mantle, and low cost tooling.

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon reading and understanding the proceeding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

I claim:

1. A golf ball comprising:

a core;

an inner cover layer disposed on said core, said inner cover layer having a thickness of from about 0.100 to about 0.010 inches, said inner cover layer comprising a blend of two or more ionomer resins, at least one of which contains no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid; and

an outer cover layer disposed on said inner cover layer, said outer cover layer having a thickness of 0.010 to 0.070 inches, and said outer cover layer comprising a polyurethane material,

wherein said golf ball has an overall diameter of 1.680 inches or more, said inner cover layer having a Shore D hardness of at least 60, and said outer cover layer having a Shore D hardness of less than 64.

2. The golf ball according to claim **1**, wherein said inner cover layer has a thickness of about 0.050 inches, and said outer cover layer has a thickness of about 0.055 inches.

3. A multi-layer golf ball comprising:

a spherical core;

an inner cover layer having Shore D hardness of at least 60 disposed on said spherical core, said inner cover layer comprising an ionomeric resin including no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi; and

an outer cover layer having a Shore D hardness of about 64 or less disposed about said inner cover layer and defining a plurality of dimples to form a multi-layer golf ball, said outer cover layer comprising a polyurethane based material and said outer cover layer having a thickness of from about 0.010 to about 0.070 inches.

4. A golf ball according to claim **3** wherein said inner cover layer has a thickness of about 0.050 inches and said outer cover layer has a thickness of about 0.055 inches, said golf ball having an overall diameter of 1.680 inches or more.

5. A multi-layer golf ball comprising:

a spherical core;

an inner cover layer disposed over said spherical core to form a spherical intermediate ball, said inner cover layer having a Shore D hardness of at least 60, said inner cover layer comprising an ionomeric resin having no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi, and said inner cover layer having a thickness from about 0.100 to about 0.010 inches; and

a dimpled outer cover layer disposed over said spherical intermediate ball to form a multi-layer golf ball, said outer cover having a Shore D hardness of 64 or less, said outer layer comprising a polyurethane, said outer cover layer having a modulus in a range of about 1,000 to about 30,000 psi, and said outer cover layer having a thickness of from about 0.010 to about 0.070 inches.

6. The multi-layer golf ball of claim **5** wherein the Shore D hardness of said outer cover layer is less than the Shore D hardness of said inner cover layer.

* * * * *

CIVIL COVER SHEET

The JS-44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON THE REVERSE OF THE FORM.)

I. (a) PLAINTIFFS
CALLAWAY GOLF COMPANY
(b) County of Residence of First Listed Plaintiff San Diego County, California
(EXCEPT IN U.S. PLAINTIFF CASES)

DEFENDANTS
ACUSHNET COMPANY
County of Residence of First Listed Defendant Bristol County, Massachusetts
(IN U.S. PLAINTIFF CASES ONLY)
NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE LAND INVOLVED

(c) Attorneys (Firm Name, Address, and Telephone Number)
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(302) 652-5070

Attorneys (If Known)

II. BASIS OF JURISDICTION (Place an "X" in One Box Only)

- ☐ 1. U.S. Government Plaintiff
- ☒ 3. Federal Question (U.S. Government Not a Party)
- ☐ 2. U.S. Government Defendant
- ☐ 4. Diversity (Indicate Citizenship of Parties in Item III)

III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff and One Box for Defendant) (For Diversity Cases Only)

	PTF	DEF		PTF	DEF
Citizen of This State	☐ 1	☐ 1	Incorporated *or* Principal Place of Business In this State	☐ 4	☐ 4
Citizen of Another State	☐ 2	☐ 2	Incorporated *and* Principal Place of Business In Another State	☐ 5	☐ 5
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IV. NATURE OF SUIT (Place an "X" in One Box Only)

CONTRACT
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- ☐ 160 Stockholders' Suits
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- ☐ 330 Federal Employers' Liability
- ☐ 340 Marine
- ☐ 345 Marine Product Liability
- ☐ 350 Motor Vehicle
- ☐ 355 Motor Vehicle Product Liability
- ☐ 360 Other Personal Injury

PERSONAL INJURY
- ☐ 362 Personal Injury--- Med. Malpractice
- ☐ 365 Personal Injury Product Liability
- ☐ 368 Asbestos Personal Injury Product Liability

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- ☐ 370 Other Fraud
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- ☐ 660 Occupational Safety/Health
- ☐ 690 Other

LABOR
- ☐ 710 Fair Labor Standards Act
- ☐ 720 Labor/Mgmt. Relations
- ☐ 730 Labor/Mgmt. Reporting & Disclosure Act
- ☐ 740 Railway Labor Act
- ☐ 790 Other Labor Litigation
- ☐ 791 Empl. Ret. Inc. Security Act

BANKRUPTCY
- ☐ 422 Appeal 28 USC 158
- ☐ 423 Withdrawal 28 USC 157

PROPERTY RIGHTS
- ☐ 820 Copyrights
- ☒ 830 Patent
- ☐ 840 Trademark

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- ☐ 861 HIA (1395ff)
- ☐ 862 Black Lung (923)
- ☐ 863 DIWC/DIWW (405(g))
- ☐ 864 SSID Title XVI
- ☐ 865 RSI (405(g))

FEDERAL TAX SUITS
- ☐ 870 Taxes (U.S. Plaintiff or Defendant)
- ☐ 871 IRS – Third Party 26 USC 7609

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- ☐ 410 Antitrust
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- ☐ 460 Deportation
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- ☐ 810 Selective Service
- ☐ 850 Securities/ Commodities/ Exchange
- ☐ 875 Customer Challenge 12 USC 3410
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- ☐ 245 Tort Product Liability
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- ☐ 440 Other Civil Rights

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- Habeas Corpus:
- ☐ 530 General
- ☐ 535 Death Penalty
- ☐ 540 Mandamus & Other
- ☐ 550 Civil Rights
- ☐ 555 Prison Condition

V. ORIGIN (PLACE "X" IN ONE BOX ONLY)

☒ 1 Original Proceeding ☐ 2 Removed from State Court ☐ 3 Remanded from Appellate Court ☐ 4 Reinstated or Reopened ☐ 5 Transferred from another district (specify) ☐ 6 Multidistrict Litigation ☐ 7 Appeal to District Judge from Magistrate Judgment

VI. CAUSE OF ACTION (Cite the U.S. Civil Statute under which you are filing and write brief statement of cause. Do not cite jurisdictional statutes unless diversity.)

Patent infringement under 35 USC §§ 271 and 281 through 285

VII. REQUESTED IN COMPLAINT: ☐ CHECK IF THIS IS A CLASS ACTION UNDER F.R.C.P. 23 **Demand: $** CHECK YES only if demanded in Complaint **JURY DEMAND** ☒ Yes ☐ No

VIII. RELATED CASE(S) IF ANY (See Instructions) JUDGE s DOCKET NUMBER

DATE February 9, 2006 SIGNATURE OF ATTORNEY OF RECORD Thomas Halkowski by Sean Hayes (#4413) TYPE NAME OF ATTORNEY Thomas L. Halkowski

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RECEIPT # ________ AMOUNT ________ APPLYING IFP ________ JUDGE ________ MAG. JUDGE ________